

Formulation-structure-property relationships for spray dried titanium dioxide

by

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i. Declaration

The candidate confirms that the work submitted is his own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

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ii. Acknowledgements

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iii. Abstract

In the process industries associated with pigments, agricultural products, food and pharmaceuticals etc, physical and mechanical difficulties are regularly encountered when conveying, handling and transporting particulate solids. These difficulties can lead to frequent stoppage of processes, loss of production time and the inefficient use of staff to restore solid flow. The diversity of material properties and the sensitivity to environmental conditions makes the prediction of bulk solids and powder handling extremely challenging. Even different grades of similar powders which have small changes to particle properties and formulation can result in major differences in bulk handling behaviour. However, for similar grades of powders, relationships between the formulation, structure and powder properties will exist. Therefore, establishing these relationships can be extremely valuable for predicting how a new grade may behave during processing.

In the manufacture of titanium dioxide (TiO_2) pigment, similar grades of powders are regularly processed for white pigments in paints, plastics and paper. Each of these different applications can require a different pigment grade, however these different grades can display major differences in their bulk handling behaviour. TiO_2 pigment is manufactured by producing a slurry of calcined 300 nm sized TiO_2 crystallites. Since the crystallites are highly agglomerated, a wet milling process is employed to fully disperse and separate the TiO_2 crystallites. Afterwards, the TiO_2 is surface treated / coated with hydrous inorganic oxides such as alumina and/or silica via a wet precipitation process. To remove accumulated salts from the coating process, the coated slurry is then filtered. Drying proceeds by employing techniques such as spray drying or spin flash drying. During these drying processes, the coated TiO_2 crystallites are assembled into granules to form a dry particulate solid. Depending on the coating type and level applied, and the drying conditions employed, the processed powder can vary substantially by the formulation and by the size and shapes of the formed granules, which creates the possibility for various bulk handling behaviours, with significant differences in powder handling characteristics such as flowability, cohesion and breakage.

In this study, three spray dried TiO_2 powders and one spin flash dried TiO_2 material were supplied by Venator, a renowned manufacturer of titanium dioxide pigment. The supplied materials had displayed major differences in powder handling behaviour, and were studied to understand the factors which influenced their bulk handling behaviour, and furthermore to establish their formulation-structure-property relationships. The formulation of the supplied materials differed by coating level, which typically varied between 0.5 – 3.5 wt%. To determine the powder characteristics, the supplied powders were initially characterised using SEM, laser diffraction, automated static image analysis, DVS and nitrogen sorption to determine powder properties such as size, shape, moisture sorption and surface area. This initial analysis revealed that the spray dried granules featured spherical geometries, whilst the spin flash dried material was irregularly

shaped. The granular morphology of the supplied materials were attributed to their respective drying methods. The particle size analysis determined the size of spray dried TiO₂ powders to be 49 – 72 µm, whilst the size of the spin flash dried material was determined to be 172 µm, as assessed by the $D[v,50]$. Moisture sorption and surface area analysis revealed that powders containing higher surface treatment levels adsorbed more moisture, which was due to the fact that a higher coating level produced a larger surface area and a greater number of sites for water molecules to adsorb to. Moisture sorption of the supplied powders were also found to be relatively low at less than 1 wt% at 40% RH which indicated the materials were relatively dry and furthermore, capillary menisci were found to be absent during SEM analysis.

To investigate powder flowability, a number of tests were employed to indirectly and directly study the flow behaviour of the supplied materials. These tests included bulk and tapped densities, compressibility tests, angle of repose, shear cell testing and FT4 powder rheology. A number of tests were required to subject the supplied powders to a range of conditions and flow regimes, as it is known that different techniques can provide different results depending on the conditions employed. Overall, the flowability of the spray dried powders were found to be governed by size and surface treatment level. A reduction in size and lower surface treatment level was found to increase cohesion, entrain air, reduce bulk density and increase compressibility, which therefore led to a reduction in powder flowability. The flowability of the spin flash dried material was found to be dominated by its larger particle size and irregular shaped granules. Larger granules were found to be beneficial for reducing cohesion and increasing bulk density. However, the mechanical interlocking of irregular shaped granules was found to increase interparticle friction, which hence impacted powder flowability.

As the van der Waal forces were considered to be the most dominant force influencing cohesion for the supplied samples, powder adhesion and cohesion was initially investigated using the drop test. The drop test showed that powders with lower levels of surface treatment were more adhesive. Afterwards, AFM was employed to investigate the contributions of the surface roughness and surface adhesion to the overall particle adhesion. The AFM analysis demonstrated that the surface roughness of the spray dried samples were similar regardless of surface treatment level. However, the AFM analysis identified differences in surface adhesion, where a surface with a low surface treatment level was found to be more adhesive. These findings were attributed to the fact that a lower surface treatment level was insufficient in providing adequate coverage to the TiO₂ surface. Consequently, a surface where more TiO₂ is exposed was more adhesive since the Hamaker constant of titanium dioxide is larger than that of alumina.

Since granule strength and breakage are structure sensitive properties, the structure of spray dried and spin flash dried TiO₂ was investigated using SEM with microtome sectioning, SEM-FIB and LF-NMR. The structural analysis revealed that the supplied granules were not hollow and were assemblies of TiO₂ crystallites held together by the surface treatment, which acted as a binder

forming solid bridges between the TiO_2 crystallites. Throughout the granule structures, networks of pores were found to be present and the porosity of the supplied granules were determined to be 24.0 – 29.3%. By applying confined uniaxial compression, the granular strength of the supplied materials were determined and were found to be dependent on granule size, coating level and porosity. A higher coating level was found to increase granule strength, whilst larger granules and a higher porosity was found to reduce granule strength. Since granule strength correlates with breakage resistance, a higher coating level will increase breakage resistance, whilst an increase in granule size and porosity will lead to a reduction in breakage resistance.

The four studies reported within this thesis have identified that spray dried particle properties, structure and formulation (surface treatment level) can be highly influential on the bulk handling behaviour of spray dried titanium dioxide. With regards to particle properties and structure, these include particle size, shape and porosity. Considering particle size, larger granule sizes are beneficial for better powder flowability and a reduction in cohesion. However, granular strength decreases with size. Therefore, unless sufficient strength can be imparted to the granules, then a compromise on granule size may be required. With regards to particle shape, spherical particles are desired for better flowability, since irregular shaped granules increase friction, which is due to the possibility of irregular shaped particles interlocking. A low granular porosity is also essential to maintain high granule strength, as these granules are likely to display a higher resistance to breakage. Therefore, control over granule size, shape and porosity should be pursued to produce powders with better handling behaviour. In terms of formulation, the surface treatments were found to influence bulk handling behaviour through two main mechanisms. The first mechanism is where higher levels of surface treatment typically 3/3.5 wt% reduce powder cohesion and improve power flowability. Whilst the 2nd mechanism is via increased granule strength and breakage resistance with higher levels of surface treatment, since these coatings were found to act as a binder. Noteworthy, is the fact that higher surface treatment levels simultaneously lead to a reduction in powder cohesion and an increase in breakage resistance, which is beneficial for improved powder handling behaviour.

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Chapter 1 – Introduction

1.1 Research introduction

Particulate solids constitute a large proportion of raw materials, intermediates and products within the process industries associated with pigments, agricultural, food, chemical, ceramic, pharmaceutical, metallurgical, plastics, other bulk powder solids and fine chemicals (Krantz et al., 2009; Francia et al., 2021). As all these materials have to be transported, conveyed or handled, there is an enormous need for information about their bulk handling characteristics. This is because many of the key performance problems of solid processing plants are associated with the physical and mechanical difficulties of handling bulk solids (Morrow, 1986). In particular, bulk handling problems can lead to frequent stoppage of processes, loss of production time and the inefficient use of staff to restore powder flow (Juliano and Barbosa-Cánovas, 2010). Furthermore, due to the diversity of material properties and the sensitivity to environmental conditions, such as the relative humidity, makes the prediction of powder handling behaviour very challenging (Ghadiri et al., 2020). Even different grades of similar powders can display major differences in their bulk handling behaviour (Carson and Pittenger, 1998). Particle science and powder technology are therefore essential to the improvements of many manufacturing processes, especially for tackling sustainability challenges such as energy consumption and waste management (Macri et al., 2020).

The bulk handling behaviour of any particulate solid is a multi-dimensional problem and can encompass attributes of powder flowability, cohesion and breakage. The terms, flowability refers to the ability of a powder to flow (Prescott and Barnum, 2000), cohesion is the property whereby particles adhere together via the interparticle forces (Li et al., 2004) and breakage is the undesirable fragmentation of particles (Bemrose and Bridgwater, 1987). Good flowability, low cohesion and high resistance to breakage are key qualities which ensure powders and other bulk solids display good handling behaviour. Each of these powder qualities can be influenced by a number of different particle properties which can include size, shape, structure, strength, surface roughness and composition, as well as other factors such as flow regime and the environmental humidity, which add to the complexity, whilst creating challenges with characterisation.

Powder flow is a complex phenomenon and can be defined as the relative movement of a bulk of particles among neighbouring particles or along a container wall surface (Juliano and Barbosa-Cánovas, 2010). In bulk material handling and processing, powder flow characteristics are vital, since they can significantly impact conveying (Ganesan et al., 2008). Powders can display a complex behaviour due to their ability to rearrange under stress (Francia et al., 2021). Generally, powder flow can be classified into four rheological states (which are also known as flow regimes);

namely a static regime where particles display no motion, a quasi-static regime dominated by frictional contacts, an intermediate regime where frictional and collisional interactions occur and a rapid granular regime which is dominated by collisional interactions only (Hassanpour et al., 2019). These flow regimes are also known to be dependent on the solid fraction of the powder and the effects of the interstitial fluid (Francia et al., 2021).

Two of the most influential particle properties which can impact powder flow are shape and size. The ideal particle geometry which facilitates a powder to flow is a sphere. Therefore, any powder featuring irregular shaped particles will have its flow properties impacted. This is due to the fact that irregular shaped particles increase friction as they have the ability to mechanically interlock (Hassanpour et al., 2019). Non-spherical particulates, such as elongated particles can also influence the distribution of the interparticle forces which can affect the powder rheology in comparison to a system of spherical particulates.

Particle size is arguably the most influential factor which can affect powder flow (Chávez Montes et al., 2019). Generally, depending on the magnitude of size, particulate materials can be split in two categories; cohesive and non-cohesive (Lumay et al., 2012). For larger particulates, the gravitational force is generally greater than the cohesive interparticle forces, and hence they normally flow easily. These powders are generally referred to as being non-cohesive. For particles less than $\sim 100\ \mu\text{m}$, the interparticle forces can be appreciable relative to gravity (Legoix et al., 2017). This is because powders of a smaller particle size have a higher degree of inter-particle contact, which translates into a higher effect of the interparticle forces between the particles, and is due to their greater surface area per unit mass. Instead of gravitational forces, the macroscopic properties of the particulate assembly are therefore mainly governed by the interparticle cohesive forces (Lumay et al., 2012). Due to their tendency to adhere to one and other, these types of powders are referred to as being cohesive. Cohesive powders are known to readily form clusters (Ghadiri et al., 2020) and can be especially problematic to handle (Li et al., 2004).

The cohesive forces can occur from a variety of sources, such as liquid bridges, electrostatics or van der Waals and as described, cohesion generally increases with a reduction in particle size (Ganesan et al., 2008). However, particle surface composition (chemistry) and surface roughness can also be influential on the strength of the interparticle force and on the number of contacts which can be formed. The surface composition influences the surface energetics and the strength of the cohesive interactions, which is especially important for the van der Waal forces. Smooth and rough surfaces provide different types of contact areas influencing the number of contacts which can be formed. For example, smooth surfaces facilitate greater contact areas, allowing greater numbers of intermolecular forces to form, which therefore results in a greater cohesive interaction (Chávez Montes et al., 2019).

During handling and conveying, bulk solids can be subjected to breakage processes which usually results in a reduction in particle size and a change in bulk density (Bemrose and Bridgwater, 1987). Hence, if breakage occurs during conveying, then a change in bulk powder handling behaviour, such as an increase in cohesion and a reduction in powder flowability can occur. For granular materials, where the individual granules are assemblies of smaller particles held together by a binding substance (Reynolds et al., 2005), a consideration of breakage is especially important. This is because the structure of these particles are often weak and friable, and hence the particle can be susceptible to breakage. To ensure a powder or bulk solid displays good handling behaviour, a high resistance to breakage is therefore a key quality. The resistance to breakage is known to correlate with particle strength (Adams and McKeown, 1996), which can be size, structure and composition sensitive. Therefore, powder characteristics such as size, structure, porosity and composition/formulation can all play a key role on the breakability and hence the bulk handling of a particulate solid.

From the above discussions, it is clear there are numerous factors which can affect the bulk handling of a particulate solid. Therefore, for any bulk handling problem, these factors, for example particle properties and powder formulation must be carefully considered to understand their influence on bulk handling characteristics such as powder flow, cohesion and breakage. One of the main reasons that bulk handling problems are so prevalent in solid processing plants can be due to a lack of knowledge about the properties of various powders. Even different grades of similar powders, which differ by small changes to composition and particle properties can display major differences in their bulk handling behaviour. However, for different grades of similar powders, relationships between the formulation, particle structure and powder properties will exist. Therefore, for similar grades of powders, establishing these relationships can be extremely valuable to the industries for predicting how a new grade may behave during processing.

In this work, the bulk handling behaviour of industrial spray dried and spin flash dried titanium dioxide pigment (TiO_2) powders are investigated in great detail and the formulation-structure-property relationships are established. The manufacture of titanium dioxide (TiO_2) pigment is an example of an industry which regularly handles different grades of similar powders where major differences in bulk handling behaviour is observed. Spray dried and spin flash dried TiO_2 powders are prepared by what is known as the wet treatment process for the preparation of TiO_2 pigment. The powders under study are actually commercial intermediates from this process and have displayed various bulk handling behaviours depending on their composition and process history. These powders were prepared by firstly dispersing aluminium doped TiO_2 in water, wet milling, followed by an aqueous coating process to deposit hydrous oxides onto the surface of the TiO_2 . Afterwards, the coated slurry was filtered, washed to remove excessive salts and then dried to produce a powder. The two commonly used drying processes, spray-drying and spin flash drying,

both form agglomerated structures of 200 nm sized titanium dioxide crystallites, and little is reported in the academic literature regarding their bulk handling behaviour. The only academic work to have reported spray dried titanium dioxide pigment is the work of Li (2019), who investigated the spray drying of unmodified TiO_2 and alumina surface treated TiO_2 . During this work, the influence of the slurry stability on the spray dried granule morphology and particle structures were considered. Examples of the spray dried titanium dioxide granules prepared by Li (2019) are shown in the SEM image of Figure 1.1. Continuing on from the work of Li (2019), this extensive study investigates the bulk handling behaviour of spray dried and spin flash dried titanium dioxide by firstly studying their powder characteristics and then later investigating in detail their flow behaviour, cohesion and breakage. By considering these bulk handling features separately, a thorough understanding of the powder properties and characteristics are obtained and an understanding of the factors which influence their bulk handling behaviour is provided. Furthermore, for spray dried titanium dioxide, the formulation-structure-property relationships are established.

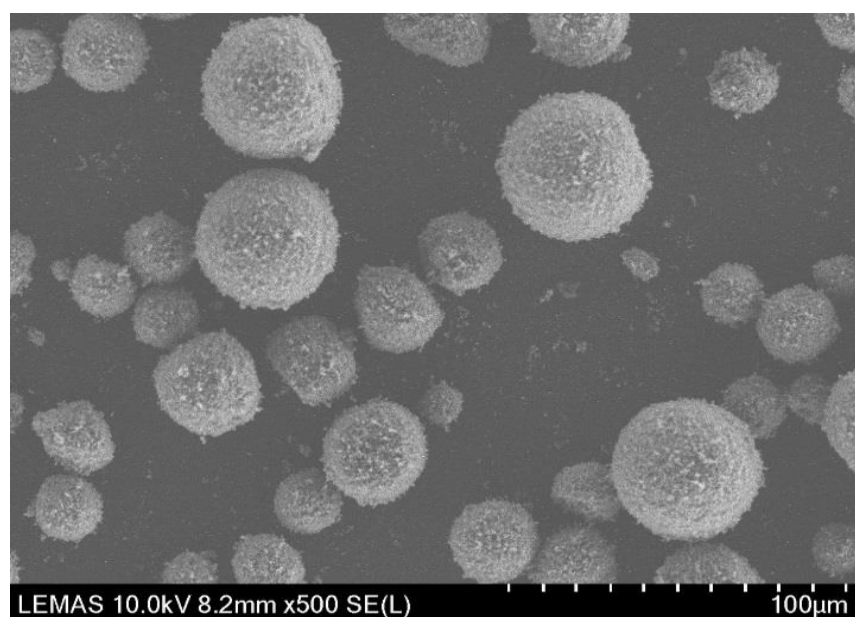


Figure 1.1 - Spray dried titanium dioxide pigment prepared by Li (2019).

1.2 Research background

Titanium dioxide pigment is manufactured by firstly dispersing aluminium doped TiO_2 in water, milling to reduce the size of formed agglomerates and then coating with hydrous oxides such as alumina, silica and zirconia. Once coated, the TiO_2 is washed to remove excessive salts and then spray dried. During the drying process, the coated titanium dioxide aggregates are assembled into

granules. The final step in the process involves a micronisation process which reduces the dried agglomerates / granules back down to the original TiO_2 crystallite size for ease of dispersion and light scattering efficiency for its intended application. In Chapter 2, an extensive review of titanium dioxide pigment and respective manufacturing processes are provided.

This research has been undertaken in collaboration with Venator (formerly Huntsmen), a global leading manufacturer of titanium dioxide pigment. The company observes significant differences in the handling properties of their powders and in particular regularly encounters a bulk handling problem in the processing of one of their spray dried powders at their titanium dioxide pigment plant located at Greatham, Hartlepool, UK. Specifically, the problem is related to the conveying of this powder as it leaves the spray drier and as it is conveyed to the bag filter.

In terms of formulation, the main difference between the powder which causes an issue and those that do not, is the level of an applied alumina surface treatment. The powder which causes this issue contains 0.5 wt% of an alumina surface treatment, whilst those that do not cause any issues contain approximately 3.0 wt% of an alumina surface treatment. Therefore, the coating / surface treatment level is an important factor to consider and in this study, its influence on the bulk handling behaviour of this material is investigated in great detail.

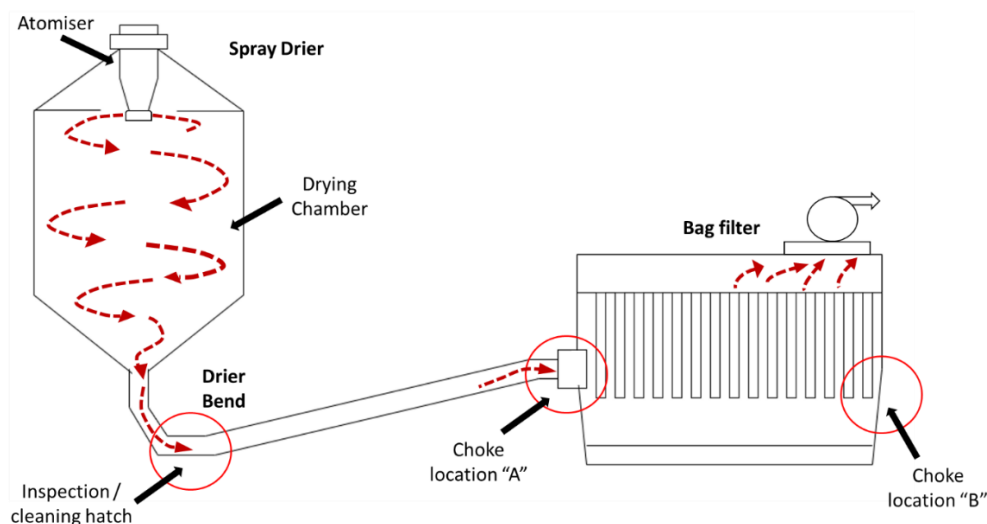


Figure 1.2 - A schematic of the spray drier bend and filter bag layout from Venators Greatham plant where the bulk handling problem occurs in the processing of spray dried titanium dioxide.

Displayed in Figure 1.2 is a schematic of the spray drier and bag filter layout where the bulk handling problem occurs. The powder in question accumulates and forms deposits at the drier bend and also forms blockages at choke locations “A” and “B”. During processing of this material,

these blockages are formed approximately weekly. This is in contrast to other powders the plant processes and conveys using the same equipment where blockages may only occur once a year. Once a blockage forms, the process has to be shut down and the material causing the blockage has to be manually removed. For the plant, this problem leads to production delays and material wastage.

Displayed in Figure 1.3 are photos taken from the bend of the spray drier (inspection/cleaning hatch) and bag filter. Figure 1.3a displays an image from outside the drier bend. The image was taken looking towards the spray drier. With the hatch door removed, a white coloured material was found coating the inside of the pipe. At the bottom of the opening, this material also forms a self-supporting bridge. Figure 1.3b and Figure 1.3c display images which were taken inside the pipe, again looking towards the outlet of the spray drier. These two images display an unusual and self-supporting structure. Apparently, bends in pipes and ducts are known to be responsible for the formation of gas-solid flow structures when cohesive powders are conveyed (Olaleye et al., 2019). Further evidence of the problem is also displayed in Figure 1.3d, which displays a photo taken inside the filter bag looking towards the bag filter inlet with a typical blockage at choke location “A”. This photo also shows typical debris which has accumulated at the filter bag inlet. Moreover, similar structures to those found in the spray drier bend were also reported to be present in the bag filter. The blockage and formation of self-supporting structures provides some clues towards the problem and the cohesive nature of this particulate material.

From the spray drier outlet bend, some of the powder debris was collected for further examination. A sample of the debris is shown in Figure 1.4. The extracted powder blocks were found to be extremely hard blocks of powder, which further indicated towards the cohesive nature of this material. It could also be postulated that to form such a hard structure, that the spray dried granules could potentially be broken down under the conveying pressure leading to the accumulation of this material and the formation of a compacted solid at the drier bend. Again, examination of this material provided further clues towards the problem and the nature of the material in question.

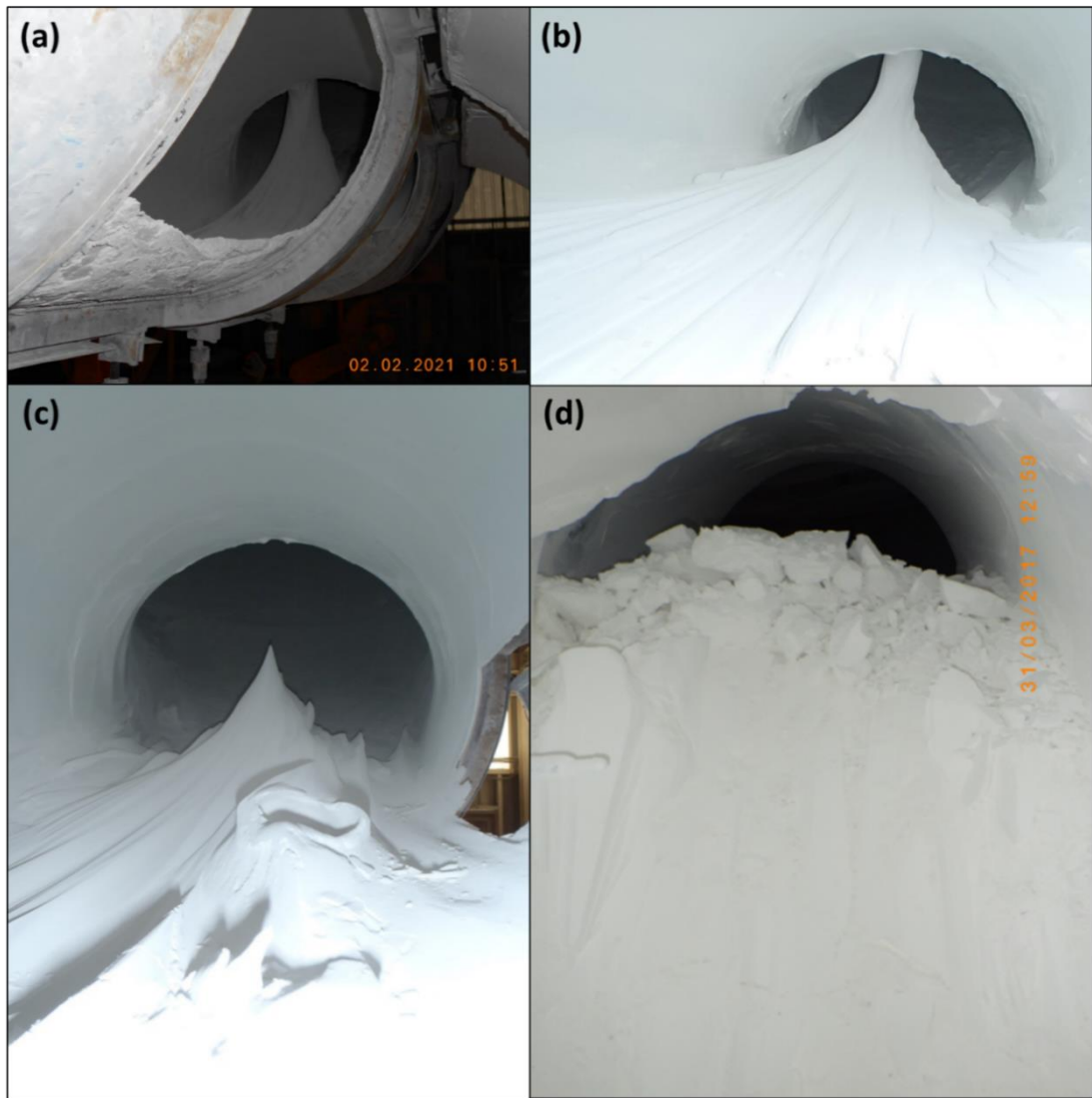


Figure 1.3 - Photos taken from outside and inside the spray drier bend (inspection/cleaning hatch) and within the bag filter (Robb, 2021). (a) An external view of the inspection / cleaning hatch, (b) and (c) display internal images looking towards the spray drier bend (d) a photo taken inside the filter bag looking towards the bag filter inlet with typical blockage at choke location "A".



Figure 1.4 - Some debris collected from the spray drier bend. Note – samples of the debris were received at Leeds and the materials were examined. During this examination, the photo shown was taken.

1.3 Aims and objectives

In the processing industries, good powder handling is a key quality often sought for a wide variety of particulate solids. Due to its significance in manufacturing, various aspects of powder handling have been the targets of extensive research efforts (Vasilenko et al., 2013). The overall aims and objectives of this research is therefore to gain a detailed understanding of the bulk handling behaviour of spray dried and spin flash dried titanium dioxide and furthermore to develop the formulation-structure-property relationships. In particular, understanding why the powder in question causes issues during conveying in comparison to other spray dried titanium dioxide powders which don't cause any issues is also important. In doing so, this research can then be used to inform effective strategies for the processing of this particulate material and provide a basis for understanding how other potential grades may behave during the future. This

information can then be used by the process industries. Moreover, this research can also be used to inform particle design and development of further titanium dioxide pigments and furthermore, this study also provides an approach for investigating the bulk handling behaviour of other cohesive powders.

In understanding the bulk handling behaviour of spray dried titanium dioxide the following questions were identified...

1. What is known in the academic literature regarding titanium dioxide pigment.
2. What are the powder characteristics of the supplied materials with regards to their size, shape, moisture sorption, surface area and structure.
3. How do these particulate characteristics influence bulk powder handling qualities such as flowability, cohesion and breakage
4. How does the composition, specifically the level and type of coating (surface treatment) influence bulk powder handling aspects such as flowability, cohesion and breakage.

1.4 Thesis structure

To meet the aims and objectives of this research, this thesis has been broken down into the following chapters.

Chapter 2 – Literature review

The literature review chapter provides essential information for understanding the materials in question, covering aspects such as pigment grades, applications, including challenges encountered by the end user and manufacturer. It is important to understand the background to the materials in order to find a potential solution to the processing of these particulate materials. Also provided in this chapter is an essential overview of the processes used to manufacture titanium dioxide pigment, including previous work undertaken on specific parts of the wet treatment process. This information is required to thoroughly understand the composition, structure and properties of the materials in question. This literature review is also focussed on understanding how the particulate material evolves as it travels through the process, which therefore aids understanding in terms of particle structures and the composition of the materials.

Chapter 3 – Powder characteristics

This first introductory study investigates the powder characteristics for the supplied materials. Characteristics of interest include size, shape, moisture sorption and surface area. The techniques utilised in this chapter are Scanning Electron Microscopy (SEM), laser diffraction, automated static image analysis and vapour sorption. Of particular interest, is particle size characterisation,

where two complementary techniques, laser diffraction and automated static image analysis are employed to properly evaluate the size of the supplied powders. This chapter also reports the essential data required to support the studies in the chapters that follow.

Chapter 4 – Powder flowability

The flowability of the supplied powders are investigated using several different techniques; bulk and tapped density, compressibility, angle of repose, shear cell testing and FT4 powder rheology. Through these measurements, the flowability for the supplied materials are investigated under a range of conditions. To provide an holistic view, the flow regimes in which some of these techniques operate in are also considered. Throughout the flowability analysis, the influence of particle properties on the observed bulk behaviour is also discussed.

Chapter 5 – Adhesion and cohesion

The factors which influence powder cohesion at the single particle scale are explored. Specifically, this chapter considers the forces which are influencing cohesion. Factors such as surface topography and surface composition which effect the levels of adhesion/cohesion displayed by each supplied material are also considered. During this work, a drop test method is employed to study particle adhesion to a substrate and Atomic Force Microscopy (AFM) is utilised to explore surface topography and surface adhesion.

Chapter 6 – Structure, strength and breakage

Investigating the particulate characteristics of the supplied materials further, the structure of spray dried and spin flash dried titanium dioxide is explored. A study of granular structure is required for understanding breakage. During this analysis, the particulate structures are investigated using three complementary techniques; SEM in combination with microtome sectioning, Low Field NMR and FIB-SEM. In the 2nd half of this chapter, the strength of the supplied materials are determined using unconfined uniaxial compression. Moreover, throughout this chapter, the influence of composition/formulation and structure is used to explain the relative strengths and the potential breakage behaviour of the supplied materials.

Chapter 7 – Conclusions and further work

The final chapter concludes by providing an overview of the bulk handling behaviour of spray dried and spin flash dried titanium dioxide. The formulation-structure-property relationships for spray dried titanium dioxide are reported and finally, suggestions for further work are provided.

Chapter 2 – Literature Review

2.1 Introduction

Titanium dioxide (TiO_2) is used to provide whiteness and opacity to a vast range of everyday products (McNulty, 2007; Gázquez et al., 2014) and is commonly used as a white pigment in paints, plastics and paper (Buchel et al., 2000; Veronovski, 2018). The global market for TiO_2 pigment is growing, it was worth \$21.4 billion in 2020, and is projected to be worth \$34.5 billion by 2030 (Market Research Future, 2021). Commercial production is done via two processes, the older sulfate process or the newer chloride process (Buchel et al., 2000). In 2008, the global production capacity reported from 58 manufacturing plants (21 chloride and 37 sulfate) was 5.9 million tonnes per annum (Auer et al., 2017) and in 2020 increased to 8.4 million tonnes (U.S. Geological Survey, 2021). The main producing countries are China, USA, Germany, UK and Japan (Merchant Research & Consulting Ltd, 2021). Some of the major players of the TiO_2 pigment market include DuPont, Tayca Corporation, Tronox Limited, Evonik Industries, CRISTAL, Huntsman International LLC, The Chemours Company Chemours, Argex Titanium Inc., Shandong Doguide Group and NL Industries (Market Research Future, 2021). Because the titanium dioxide market is lucrative, many companies are spending millions, if not billions, on research and development. For example, the major American company DuPont Inc managed to retain its superior position by investing heavily in research and development, which has allowed the company to produce titanium dioxide pigment with much lower price points.

The wide use of TiO_2 is due to its superior light scattering properties when compared to other white pigments such as zinc oxide, zinc sulfide, and lithopone (Auer et al., 2017). To improve their performance in many end-user applications, TiO_2 pigments are generally coated (Tyler, 2000). The coating process is also known as the finishing or aftertreatment process (Auer et al., 2017). The coating process consists of several steps and includes; dispersion, milling, coating, filtration and washing, drying, micronizing and packing (Thompson, 1995). During dispersion, chloride or sulfate produced TiO_2 is slurried in water, with or without dispersing agent. Afterwards, the slurry is milled to reduce or eliminate agglomerates. Later in the process, the TiO_2 is coated by precipitating white hydrated oxides onto the pigments surface. Drying proceeds and the pigment is subjected to a final micronization step (Tyler, 2000). During micronization, the pigment may also receive an organic surface treatment (Veronovski, 2018).

The surface treatments applied to TiO_2 have been recognised to change the pigments bulk handling behaviour. For example, hydrous alumina is known to improve pigment dispersibility (Tyler, 2000), whilst unmodified (pigment TiO_2 without inorganic coating) chloride pigment is known to cake and exhibit poor flow behaviour (Braun et al., 1992). Furthermore, the reliability

of powder handling operations is known to be sensitive to the level of coating. For example, in one plant a pneumatic conveying line was observed to block once a week for a lightly coated pigment in comparison to once a year for a heavily alumina coated pigment (Robb, 2020). TiO_2 is also generally known to have a bad reputation for its problematic powder handling (Thompson, 2017). These problems can include the formation of rat holes and bridges in hoppers where blockages may occur (Flexicon, n.d.) and difficulties in conveying where equipment such as screw conveyors can stall and ultimately fail (Spiroflow, n.d.). The occurrence of blockages ultimately leads to equipment shutdown while the obstruction is removed, elevating the risk of dusting and spillage (Flexicon, n.d.). Therefore to ensure reliable flow, constant maintenance is required (Marinelli, 2013). In general, powder handling problems lead to production delays, reduce process efficiency and increased operating costs (Altair, 2020). The poor flowability of TiO_2 is thought to stem from its small particle size, irregular shapes and high cohesiveness (Thompson, 2017).

This research is ultimately aimed at solving a processing problem in the manufacture of titanium dioxide pigment. Therefore, in order to solve such a problem, it is necessary to understand how titanium dioxide pigment is manufactured. Since the composition of the pigment varies for different applications, it is also essential to understand various TiO_2 pigment grades and the challenges which are involved in their manufacture and end use. This literature review discusses these important aspects. Also provided in this review are specific studies related to the materials under study. Section 2.5 discusses aluminium doped TiO_2 , polyphosphate dispersants and milling. Section 2.6 provides an overview of alumina, silica and zirconia surface treatments, whilst Section 2.7 provides a review of work related to the spray drying of pigment TiO_2 . For the research presented in the proceeding chapters, the manufacturing sections are focussed on understanding how this particulate material evolves as it travels through the process. In doing so, this information provides a basis for understanding the characteristics of the materials under study and the methods and approaches utilised in this research.

2.2 Titanium dioxide pigments, applications and challenges

Titanium dioxide provides whiteness and opacity to a substantial number of everyday products (Parfitt, 1980; McNulty, 2007) and is commonly used as a white pigment in paints and coatings, printing inks, plastics and paper (Buchel et al., 2000). Titanium dioxide also finds use in glass, rubber, fibre, enamel and ceramics, cosmetics, food and pharmaceutical industries (Gázquez et al., 2014). The exclusive use of titanium dioxide as a white pigment is owed to its high refractive index ($n \approx 2.7$), which is much higher in comparison to other white pigments such as zinc oxide ($n = 2.0$) and china clay ($n = 1.6$) (McNulty, 2007).

For a given application/industry and for optimum performance, a specific grade of pigment is required. Pigment grades vary by TiO₂ type and applied surface treatments (Veronovski, 2018). Each different pigment grade provides an optimum set of properties for a given application. For all grades of pigment, TiO₂ serves as the optically active ingredient and all pigment grades contain 80% or more TiO₂ (Braun et al., 1992). The TiO₂ can vary in both crystalline phase and crystallite size, but also by the process used to prepare the TiO₂.

The TiO₂ crystalline phase varies by either the anatase or rutile forms (Braun et al., 1992). These two phases differ by their refractive indices (rutile: $n = 2.7$, anatase: $n = 2.5$), density (rutile: 4.3 g/cm³, anatase: 3.8 g/cm³) and chemical stability (Auer et al., 2017). With regards to chemical stability, the rutile phase is known to be more thermodynamically stable than the anatase form. The rutile phase tends to scatter more light than the anatase phase and is therefore exclusively used in paints and coatings, whilst due to their lower density, anatase grades are preferred in the paper industry (Braun et al., 1992). Rutile pigments are also known to be more abrasive than anatase pigments (Auer et al., 2017). This is due to the fact that rutile has a higher density and a more compact atomic structure in comparison to anatase. Consequently, the Mohs hardness of rutile (6.5-7.0) is much higher than anatase (5.5-6.0). The relative hardness of rutile and anatase can also be influenced significantly by additives.

The light scattering power of TiO₂ pigment is dependent on particle size and for TiO₂ its maximum is at a particle size of 200 nm (Buchel et al., 2000). Therefore, the process for synthesizing TiO₂ is optimised to produce TiO₂ crystallites with crystallite sizes of 100-300 nm (Buxbaum, 1998; McNulty, 2007). The mean TiO₂ crystallite size is also tailored to the required optical performance. Smaller crystallite sizes are known to scatter more blue light providing a blue undertone, whilst the intermediate and larger crystal sizes scatter more yellow and red light respectively, providing yellow and red undertones (Gázquez et al., 2014; Veronovski, 2018). For the colouring of plastics, slightly smaller crystallites are also preferred (Auer et al., 2017). The pigment crystallites are also known to have a spherical shape, the size distribution is quite narrow and a size of 200 nm usually corresponds to a surface area of approximately 10 m²/g (Parfitt, 1980).

The TiO₂ utilised in different pigment grades is manufactured by either the chloride process or the sulfate process, see later in Section 2.3 (Buchel et al., 2000). The sulfate process produces both anatase and rutile, whilst the chloride process only produces the rutile form. In terms of composition, there are subtle differences between sulfate and chloride produced TiO₂. Sulfate produced TiO₂ can contain up to 0.3% niobium pentoxide, 0.3% phosphorus pentoxide and 0.2% alumina. The niobium pentoxide and phosphorus pentoxide are impurities and come from the ore in which the TiO₂ was made from, whilst the alumina is added to compensate for these impurities

minimizing discoloration. In contrast, Chloride pigments are much purer and contain fewer unwanted impurities (Braun et al., 1992). Sulfate pigments are used in the paper industry, whilst chloride pigments are preferred in the high-temperature processing of plastics. For many applications, chloride and sulfate pigment can be interchangeable, whilst for other applications, the better scattering power, greater durability, superior brightness and more neutral masstone of chloride pigments are favoured. However, sulfate pigments are less abrasive and are therefore favoured for fibre and printing ink applications (Auer et al., 2017).

TiO₂ is a strong absorber of UV light (Parfitt, 1980). This can be beneficial as the TiO₂ can help to protect paint films, however TiO₂ is also a UV-activated oxidation catalyst and can therefore degrade polymeric matrices/binders in which the TiO₂ is dispersed in (Braun et al., 1992). This destructive effect of TiO₂ is commonly called chalking and can be controlled in two ways (Buchel et al., 2000). The first is through the use of rutile rather than anatase, since rutile has lower photoactivity. The 2nd method is by encapsulating the TiO₂ particles in an inorganic coating. In the absence of a coating, a paint film containing unmodified TiO₂ in the presence of air, water and sunlight would degrade rapidly and discolour. The surface coatings therefore avoids this discolouration by preventing the close contact between the reactive surface of the TiO₂ and the matrix in which the TiO₂ is dispersed in (Veronovski, 2018).

The most common surface treatments/coatings applied to TiO₂ pigment are alumina, silica and zirconia (Bugnon, 1996; Tyler, 2000). For specialty applications, a number of other inorganic surface treatments are sometimes used. These treatments can include tin oxide, zinc oxide, cerium oxide, phosphate and nitrate. These treatments are most commonly precipitated in layers, however, some of the components can also be co-precipitated to change the surface characteristics of the pigment (Tyler, 2000).

Hydrous aluminium oxide (alumina) is probably the most common surface treatment applied to TiO₂ pigment and when multiple treatment layers are deposited, alumina is most often the final layer. The hydrous alumina may be present as either the amorphous or pseudo-boehmite form. As well as reducing photoactivity, hydrous alumina also improves pigment dispersibility (Tyler, 2000). The presence of hydrous alumina is thought to decrease the inter-particle forces by lowering the van der Waals forces by several orders of magnitude (Braun et al., 1992). Hydrous aluminium oxide phases also appear to improve dispersibility more effectively than most other hydroxides and oxides which are used (Allen et al., 2004). To aid dispersion, up to 5% of hydrous alumina can be precipitated on to the surface of TiO₂ (Jacobson, 1983). Hydrous alumina also acts as a spacer between TiO₂ pigment particles improving gloss and pigment opacity (Tyler, 2000). The amorphous form of alumina also provides a moderate amount of durability in terms

of weatherability and lightness, but the pseudo-boehmite form is known to be a more effective spacer (Tyler, 2000).

Depending on the surface treatment conditions employed (see later in Section 2.5), a silica surface treatment featuring a “fluffy” morphology or a dense glassy encapsulating shell can be formed on the surface of TiO_2 . The “fluffy” coating provides better spacing, optical efficiency, increased oil adsorption and reduced gloss. Consequently, these pigments are used in matt, dry-hiding formulations. In contrast, the dense glassy silica encapsulating shell provides the highest durability, with the level of durability increasing with coating level (Tyler, 2000; Veronovski et al., 2014). Super durable grades of pigment can contain up to 4% silica or more by weight on TiO_2 (Braun et al., 1992). A disadvantage of silica surface treatments is that they can reduce whiteness and gloss to a certain extent and therefore, are unsatisfactory for some applications (Li et al., 2010).

Zirconia surface treatments are also used to improve pigment durability (George et al., 2015). Depending on the amount of zirconia applied, the durability is usually in the moderate to high category (Tyler, 2000). A great advantage of zirconia is its ability to improve durability without significantly impacting pigment optical properties. The majority of zirconia surface treated pigments also provide very good gloss.

The level of the surface treatment applied and hence TiO_2 content tends to vary for different applications. Pigments intended for emulsion paints tend to contain approximately 80-85% TiO_2 , with a silica content up to 10% (Auer et al., 2017). For general-purpose paints, coatings consist of 2-5% alumina or alumina and silica. If greater resistance to weathering is desired, the pigments are coated more heavily to about 7-10% (Allen et al., 2004) and highly weather-resistant types are coated with up to 15% silica or zirconia (Veronovski et al., 2014). Pigments intended for the paper laminate industry tend to contain a TiO_2 content of ~90% with surface coatings of silicates or phosphates of titanium, zirconium and aluminium (Auer et al., 2017). For colouring of plastics, usually smaller TiO_2 particles are used with typically less than 3% inorganic coating. The pigment typically has a TiO_2 content of >95% (Day, 1990) with an aftertreatment of 1 - 3% alumina (Auer et al., 2017). In comparison to paints, plastics have a lower level of surface treatment applied. This is because polymers and polymer blends are processed at temperatures at which the inorganic coatings on pigments starts to dehydrate (Day, 1990). The evolved moisture can then react with moisture sensitive polymers such as polycarbonates and nylon, causing lace curtaining or the formation of bubbles in the finished plastic part. These effects can then impact the final properties of the plastic such as its tensile strength.

Besides inorganic constituents, most uncoated and many coated pigments also contain up to 0.5% of an organic compound (Braun et al., 1992). The organic compound has two functions. The first

is to improve processing by improving the flow of the pigment in the micronizer / fluid-energy jet mill. Further discussion of the micronization process is provided later in Section 2.4. In doing so, the pigment experiences a more uniform grind. The grinding aids are usually polyhydroxy compounds, for example, pentaerythritol, trimethylol propane or triethanolamine. The second purpose of the organic is to improve compatibility and dispersibility with its intended use (Tyler, 2000; Lim et al., 2008). Alternatively, a silicon or phosphate compound can also be used for the same purpose. The organic also helps to reduce agglomeration, especially during storage of the pigment (Tyler, 2000). A further advantage of organic surface treatments is that they also reduce water adsorption, which is again important for the processing of plastics (Tyler, 2000; Lim et al., 2008). The nature of the organic compound(s) used depends on the intended use of the pigment (Auer et al., 2017). The pigment surface can be made either hydrophobic, for example by using silicones, organophosphates, and alkyl phthalates or hydrophilic, for example by using alcohols, esters, ethers and their polymers, amines or organic acids. Also combinations of hydrophobic and hydrophilic substances may also be used for obtaining tailor-made surface properties.

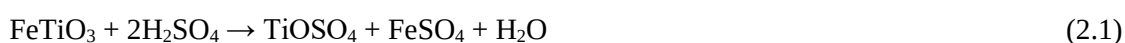
The requirements for different grades of pigments containing various surface treatments for different applications can also impose challenges with regards to manufacturing. This is particularly important in terms of powder handling when the pigment needs to be transported from the drier to the micronizer and from the micronizer to the packing equipment. The surface treatments applied to TiO_2 have been recognised to change the pigments bulk powder handling behaviour. For example, hydrous alumina is known to improve pigment dispersibility (Tyler, 2000) and uncoated titanium dioxide pigments are known to be very cohesive and have high tensile strengths (Parfitt, 1980). The surface coating has been recognised to reduce this effect allowing the powder to be easily dispersed (Parfitt, 1980). Unmodified chloride pigment has been identified to cake and exhibit poor flow behaviour (Braun et al., 1992) and moreover, a pneumatic conveying line has been known to block once a week for a lightly coated pigment in comparison to once a year for a heavily alumina coated pigment (Robb, 2020). Powder cohesion and agglomerate strength is also increased by the presence of surface moisture. The surface moisture is thought to increase cohesion through the formation of water bridges between pigment particles (Parfitt, 1980). However in reality, there are a huge number of other factors which can influence TiO_2 powder cohesion and ultimately bulk powder handling behaviour. This research thesis explores and investigates these important aspects.

2.3 TiO_2 production

Titanium dioxide pigment is manufactured using two different processes, the so called sulfate and chloride routes. Both routes are in effect chemical purifications, where an impure TiO_2 feedstock is converted to an intermediate, with separation of impurities and then transformation of the

intermediate to pure TiO₂ pigment (McNulty, 2007). Moreover, the sulfate route utilises concentrated sulfuric acid, whereas the chloride route employs chlorine gas. The sulfate process was the first commercialized technology to obtain titanium dioxide pigment and the newer chloride process was then later commercialized by Du Pont in the early 1950s (Gázquez et al., 2014). The sulfate process accounts for approximately 40% of the worlds TiO₂ production, whilst the chloride process accounts for the other 60% (Gázquez et al., 2014).

The overall chemistry of the sulfate process can be represented in Equations 2.1, 2.2 and 2.3 (McNulty, 2007; Gázquez et al., 2014).



The raw feedstock materials such as ilmenite or titanium slag are first digested with strong sulfuric acid at a temperature of 150-220°C (Auer et al., 2017). During digestion, the titanium components are converted into titanyl sulfate and the iron into sulfates, Equation 2.1. A clarification process is then used to remove any undigested material from the titanyl sulfate containing liquor. A hydrolysis step proceeds whereby the titanyl sulfate is reacted with water to produce a hydrated titanium dioxide product with the release of sulfuric acid, Equation 2.2 (McNulty, 2007). During hydrolysis, the hydrated titanium dioxide is precipitated at temperatures of 94-110°C to form particles with a size of approximately 5 nm (Auer et al., 2017). The hydrated TiO₂ is then sent forward to a rotary kiln where it is calcined to produce the anhydrous titanium dioxide product, Equation 2.3 (McNulty, 2007). This compound can be calcined at 650-1000°C to form either the anatase or rutile type titanium dioxide (Middlemas et al., 2015). During calcination, pigment particles are formed with a typical size of 200 nm (Auer et al., 2017).

The overall chemistry of the chloride process can be represented as Equations 2.4 and 2.5 (McNulty, 2007; Gázquez et al., 2014).



The chloride process begins by mixing the raw feed materials with gaseous chlorine at a temperature of around 900-1000°C. This initial chlorination step takes place in a fluidized bed reactor in the presence of coke as a reducing agent. A gas stream containing titanium tetrachloride (TiCl₄), oxides of carbon and other metal chlorides are produced, Equation 2.4. The metal chlorides are formed from the impurity metals of the feedstock and to separate the impurities out, the gas stream is cooled with recycled liquid TiCl₄. This reduction in temperature causes the

impurities to condense. The purified TiCl_4 vapour is then sent forward and condensed to form pure liquid TiCl_4 where it is then fed to a high temperature oxidation reactor and oxidised at a temperature of 1500°C to form titanium dioxide, Equation 2.5. The chlorine gas which is released is then recycled back to the beginning of the reaction to produce more TiCl_4 (McNulty, 2007; Gázquez et al., 2014). During oxidation, an aluminium dopant in the form of aluminium tri-chloride is also introduced in small amounts (0.2 - 2.0 wt%) to promote the formation of the rutile crystalline phase (Akhtar et al., 1994; Hartmann, 1996; Auer et al., 2017). The final concentration of alumina in the pigment is approximately 1% (Braun et al., 1992).

2.4 Coating process

The coating process is used to modify the surface of TiO_2 pigment with inorganic and organic compounds. The surface treatment process consists of several steps and includes dispersing, stabilising and milling TiO_2 , which is then followed by coating, filtration and washing, drying and micronization (Thompson, 1995).

The surface treatment process begins by producing a slurry of the uncoated base pigment from the chloride oxidizer or the sulfate calciner in water (Braun et al., 1992; Reck and Richards, 1997; Tyler, 2000). During this dispersion process, any remaining residual chlorine is reduced or residual acid is neutralized (Braun et al., 1992). Sometimes the dispersion is allowed to settle to remove any oversize particles (Reck and Richards, 1997). To aid the dispersion process, phosphate, silicate or organic dispersants are sometimes introduced (Thompson, 1995).

The TiO_2 pigment then undergoes wet milling which reduces or eliminates the agglomerates in the base pigment. These agglomerates are formed during oxidation or calcination processes during synthesis of the TiO_2 (Tyler, 2000). Hence the milling process is used to deagglomerate and produce the best possible particle size. This is usually achieved using ball, media or sand mills (Tyler, 2000). During media or sand milling, millimetre sized grinding media are cascaded over the pigment agglomerates, grinding them into individual crystallites (Braun et al., 1992). The milling process usually reduces the agglomerate size down to less than a micrometre (Braun et al., 1992). If a sand mill is employed, the slurry is passed through a hydro-cyclone to remove any residual sand (Sutcliffe, 2018). The milling step is also known to reduce the intensity of the final micronization process and is therefore widely practiced (Braun et al., 1992; Tyler, 2000).

During the wet treatment process, the coatings are precipitated from aqueous solutions onto the suspended TiO_2 particles (Braun et al., 1992; Auer et al., 2017). Precipitation of inorganic oxides from solution occurs via the hydrolysis of acidic or basic salts (Li et al., 2010). Coatings of widely varying compounds can be produced and as previously mentioned, the most common are oxides,

oxide hydrates, silicates, and/or phosphates of titanium, zirconium, silicon, and aluminum (Auer et al., 2017; Veronovski, 2018). For special applications, boron, tin, zinc, cerium, manganese, antimony, or vanadium compounds are sometimes used (Auer et al., 2017). Inorganic surface treatments such as alumina and silica can be precipitated in single layers, or co-precipitated on the surface of TiO_2 , for example aluminosilicates or by forming a double layer by depositing one layer over the other, for example a double layer of silica and alumina (Braun et al., 1992). The coating procedure tends to occur using batch processes in stirred tanks (Buxbaum, 1998; Auer et al., 2017). Continuous precipitation is also sometimes used in mixing lines or cascades of stirred tanks (Auer et al., 2017). Controlled temperature and pH cycles are used to deposit small amounts of oxides onto the uncoated base (Thompson, 1995). The morphology and the crystal structure of the surface treatment layers are highly influenced by temperature, pH, deposition rate, source chemicals and other factors (Tyler, 2000; Veronovski et al., 2014). The coatings are usually 10 nm in thickness, are not always uniform, and may not always completely cover the available surface (Parfitt, 1980). Alumina is probably the most common surface treatment applied to TiO_2 pigment (Braun et al., 1992; Lim et al., 2011). Various reagents can be used for its deposition, e.g., sodium aluminate, which reacts with acid or aluminium sulfate, which reacts with base. If sodium aluminate or aluminum sulfate are added to a neutral slurry, an amorphous gel initially forms. When the gel is allowed to stand, a pseudo-boehmite structure can form. Apparently, Pseudo-boehmite is known to crystallize with a ribbon-like morphology (Braun et al., 1992).

After receiving a surface treatment, the product is filtered, washed and dried (Braun et al., 1992). During washing, excessive salts from the wet treatment process are removed (Auer et al., 2017). Washing of coated TiO_2 pigments is usually undertaken on plate and frame filters, press belt filters or 2-3 drum filters operated in series (Gesenhues, 2003). With drum filtration, the production capacity is often limited by a thin filter cake, however in contrast to press filtration, the cake is easily washed and redispersed afterwards for drying (Gesenhues, 2003).

Many methods can be used to dry TiO_2 pigment. These methods may include belt, spray, spin flash or fluidised-bed dryers (Sharafudeen, 2012; Auer et al., 2017; Farooque et al., 2020). In the drying of TiO_2 , the following factors are usually considered; the cost of heat energy for drying, improving product quality and ensuring a low residual moisture in the dried product. In fact, according to Marchevskii and Grobovenko (2018), the process of drying TiO_2 is the most energy-intensive and limiting process in TiO_2 production technology. This research is mostly concerned with TiO_2 pigment powders prepared by spray drying and spin flash drying. Therefore, our discussion of drying techniques will be limited to spray drying and spin flash drying only.

During spray drying, the washed surface treated dispersion is pumped to an atomiser located inside a drying chamber. The atomiser converts the dispersion into a continuous fine spray of

micrometre sized droplets. Hot air is continuously circulated through the chamber and the droplets are rapidly dried to form granules. The final powder is then separated from the drying gas and collected by a cyclone or filter bag.

The spin flash drying process involves the transport of a feed material into a drying chamber using a mechanical wet feeder unit. The wet feeder unit is used to help disperse a high-viscosity paste or filter cake whilst transporting the wet feed particles into a drying chamber. The wet feed material falls vertically and comes into contact with a spinning rotor, where dispersion and break-up of the wet feed material then takes place. This method of dispersion contrasts with the spray drier which utilizes an atomizer. Hot air enters from the bottom of the drying chamber and spirals upwards. As the hot air leaves the top of the chamber, dried granules are removed, whilst the heavier wetter particles remain in the chamber (Mujumdar, 2014). Examples of a co-current spray drier and spin flash drier are shown in Figure 2.1.

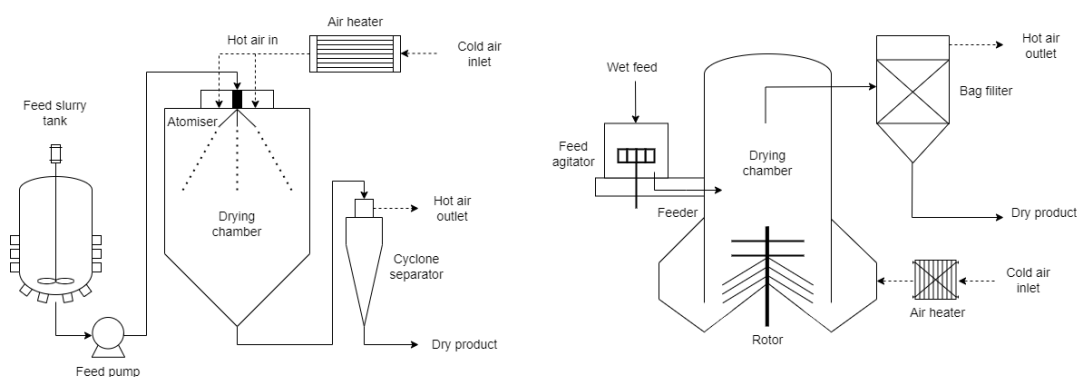


Figure 2.1 - Examples of a co-current spray drier (left) and a spin flash drier layout (right). Redrawn and adapted from Mujumdar (2014).

After drying, the pigment is subjected to the final micronization step, which is normally undertaken using a micronizer / fluid energy mill (Tyler, 2000). The intensity of the micronization which is needed to produce the optimum pigment properties depends on the base pigment, initial milling, and treatment. If initial milling is used, the micronization step serves to break up the agglomerates formed during coating and drying process (Tyler, 2000). However, without the initial milling step, then micronization would also need to be intense enough to break up the agglomerates formed during oxidation or calcination (Tyler, 2000). Fluid energy mills can efficiently break pigment agglomerates into single crystals of pigmentary dimensions (Braun et al., 1992). Micronizers consist of a disk-shaped chamber where steam and pigment are injected tangentially at supersonic speeds. The impact of pigment agglomerates with the wall of the micronizer leads to fracture and attrition (Braun et al., 1992). Fluid energy mills not only grind

the pigment but also classifies the particles. In order to achieve a uniform grind and good classification, the pigment must flow at a uniform rate into the micronizer so that the flow pattern is not disturbed. (Braun et al., 1992). Thus, micronizing aids are used to improve dry powder flow. Compounds such as polyhydroxy compounds are usually utilised (Braun et al., 1992). As previously stated, these organic compounds can also improve pigment dispersibility in a variety of media (Reck and Richards, 1997).

2.5 Al-doped TiO₂, milling and polyphosphate dispersants

The materials under study have been prepared from aluminium doped TiO₂ (Al-doped TiO₂) synthesised via the chloride process, sodium hexametaphosphate (SHP / SHMP) dispersants have been introduced and the slurry has been milled prior to coating and drying. Therefore, in the sections that follow, some works which have investigated specific attributes of these materials are discussed as they are thought to reveal some of the finer details of the materials under study whilst providing further insights to the process.

2.5.1 Al-doped TiO₂ and milling

Displayed in Figure 2.2 is an example of a Transmission Electron Microscopy (TEM) image of aluminium doped TiO₂ which has been milled for 1 minute. According to the works of Austin et al. (2021) and Taylor et al. (2003) there is a discrepancy in the literature regarding the location of the aluminium dopant within Al-doped TiO₂. Some authors claim that the Al-dopant resides to a greater degree at the surface, whereas others suggest it lies within the bulk of the pigment. The materials investigated in these works were sourced from sulfate and chloride processes, some pigments were formed through the use of additives, both anatase and rutile forms were studied and furthermore, some pigments had been subjected to milling (Garbassi et al., 1987; Johansson and Losoi, 1991; Gesenhues, 1997; Taylor et al., 2003; Tsai et al., 2012; Austin et al., 2021). Due to the different methods of preparing the TiO₂ before undertaking any analysis, it is therefore difficult to draw any conclusions from these works with regards to the location of the Al-dopant. This is because during the different methods of synthesis, the use of additives and the presence of any impurities may influence the location in which the aluminium dopant forms in the TiO₂ crystallite. Furthermore, in the latest work of Austin et al. (2021), see discussion later, showed that the extent of milling can also affect the amount of Al-dopant concentration at the surface of the pigment. In this work, we are only interested in rutile TiO₂ produced from the chloride process. The preceding discussions will therefore focus on chloride produced rutile TiO₂, which includes the works of Taylor et al. (2003) and Austin et al. (2021). Moreover, the work of Austin et al. (2021) provides insights towards the intricacies of the milling process.

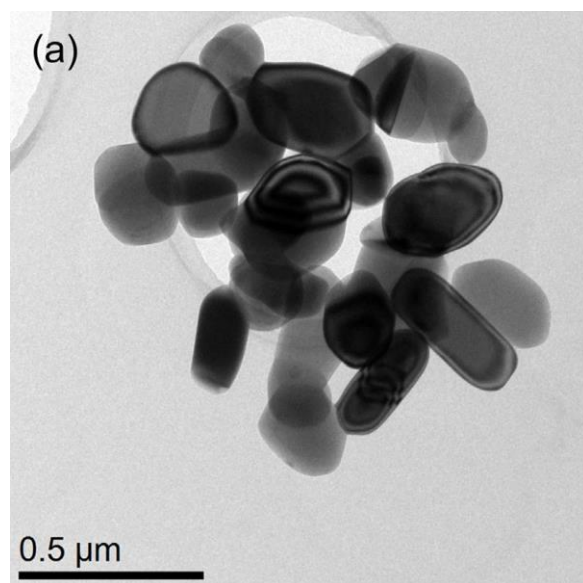


Figure 2.2 - TEM image of aluminium doped TiO_2 which has been milled for 1 minute (Elliott et al., 2019).

Taylor et al. (2003) studied four aluminium-doped rutile pigment samples with varying bulk aluminium concentrations which had been prepared using the chloride process. This study did not mention if the TiO_2 had been milled. The bulk alumina concentrations were found to vary between 0.33 to 1.18 wt% which equates to an aluminium concentration of ~ 0.1 to 0.4 wt%. The composition, electrochemistry and rheology of the supplied pigments were investigated. The composition analysis suggested there was a very large concentration of aluminium present at the surfaces of the pigment particles relative to the core concentration. The electrochemistry results showed that all pigments had an iso-electric point (iep) between pure rutile ($\text{pH}_{\text{iep}} 4.9$) and pure alumina ($\text{pH}_{\text{iep}} 9.2$) indicating that the surface of the pigments were heterogenous consisting of titanium and aluminium hydroxide groups. Furthermore, it was observed that the pH at which the iep occurs increased with increasing aluminium surface concentrations. The rheology of the pigment was found to be largely dictated by the suspension pH and surface chemistry and hence was controlled by the repulsive electrostatic and attractive van der Waal forces. The maximum yield values for the pigments were also found to correspond with the pH_{iep} values and the yield stress was also found to decrease with increasing surface aluminium concentrations. As the Hamaker constant for rutile and alumina in water (A_{131}) are 6.0×10^{-20} and 2.75×10^{-20} J respectively, these results were therefore attributed to a reduction in the composite Hamaker constant of the pigment with increasing aluminium concentration.

The work of Austin et al. (2021) investigated the change in surface chemistry of Al-doped TiO_2 particles during stirred wet media milling. Al-doped TiO_2 samples were milled at stirrer speeds

between 2500 – 8000 rpm over different time periods up to 60 mins. Over time, a reduction in particle size and an increase in specific surface area (SSA) was observed and consequently was attributed to the de-agglomeration and particle breakage processes. Zeta potential measurements were undertaken on non-milled and milled samples taken at intervals during the milling process. The non-milled sample was determined to have an iso-electric point at pH 5.7 and was found to be in good agreement with rutile TiO_2 , which generally has an iso-electric point between pH 4 and 6. The determined iso-electric points for the milled samples were found to increase to a maximum of pH 8.1 during milling. As the iso-electric point of alumina has a value of pH 9, these results suggested the milling process led to the alumina being exposed, which was initially present under the surface. Aluminium surface concentrations were also measured by XPS for non-milled and milled samples and results were found to be consistent with determined iso-electric points. Linear correlations between the iso-electric point pH, SSA and aluminium surface concentrations were also found, with the exception of samples milled at the highest stirrer speed of 8000 rpm. Instead, significantly higher SSA's and much lower iso-electric point pH's were determined and were attributed to the presence of many spherical ultra-fines (<50 nm) which surface coated the larger pigment particles. These ultrafine particles were also observed by Elliott et al. (2019) for samples which had been milled for prolonged times. Elliott et al. (2019) also showed that these fine particles exhibited a rutile TiO_2 crystal structure. The reduced iso-electric point for 8000 rpm milled samples were therefore accredited to these fine particles which have titania surface properties and consequently screened the true surface potential of the larger pigment particles. Therefore, a change in milling behaviour was thought to be induced at 8000 rpm under very high shear conditions. Overall, the work of Austin et al. (2021) showed that the aluminium-doped TiO_2 particles were initially titania surface-rich and the bulk alumina became increasingly exposed during the milling process.

With regards to the location of the Al-dopant, the study of Taylor et al. (2003) and Austin et al. (2021) provide different findings. The study of Taylor et al. (2003) suggests that the surface of the pigment could be rich in alumina, whilst the work of Austin et al. (2021) suggests that the Al-dopant resides under the surface and becomes exposed during the milling process. For this study, knowledge of the surface composition of the materials under study is important, as it is likely to influence interparticle cohesion and powder flow in a similar way as the surface composition effects suspension rheology. Furthermore, since the location of the aluminium dopant is not known, these findings must be held in mind when interpreting results where surface composition may play an important role.

2.5.2 Polyphosphate dispersants

Polyphosphates are often added to the titania pigment suspension during processes such as milling, in order to improve dispersion properties and reduce suspension viscosity (Elliott et al., 2019). In wet stirred milling of Al-doped TiO_2 , sodium hexametaphosphate (SHMP) is used as a small molecule dispersant to improve milling performance (Austin et al., 2022). Polyphosphates such as SHMP have the ability to adsorb onto metal oxide and clay particle surfaces via electrostatic and/or chemisorption mechanisms (Taylor et al., 2003; Farrokhpay, 2009). Chemisorption dominates polyphosphate adsorption at pH 9, whilst a combination of chemisorption and electrostatic interactions occurs at pH 4 (Taylor et al., 2003). Electrostatic adsorption is thought to occur between the negative phosphate groups and positive sites (MOH_2^+) at the particle surface (Taylor et al., 2003). Chemisorption occurs between the polyphosphate and metal oxide forming a probable bridging bidentate surface complex through Ti-O-P bonds (Taylor et al., 2003). According to Connor and McQuillan (1999) and Michelmore et al. (2003), polyphosphate dispersants bind to the surface of TiO_2 as a bidentate ligand. However, the way in which polyphosphate dispersants bind to the surface of TiO_2 can be different and depends on the number of phosphate groups. Connor and McQuillan (1999) and Michelmore et al. (2003) proposed that orthophosphates ($P_n = 1$) form Ti-O-P bonds from the same phosphate group, whereas polyphosphates form two single Ti-O-P bonds from the terminal phosphate groups and consequently results in the polyphosphate lying parallel to the surface (Figure 2.3). Elliott et al. (2019) characterised milled polyphosphate absorbed aluminium-doped TiO_2 and showed that an increase in milling time led to the absorption of more SHMP onto the alumina-doped pigment surface due to the breakage of agglomerates/aggregates. In terms of this study, these findings are important due to the fact that the polyphosphate chemisorbs to the surface of the TiO_2 and is therefore likely to be present in the materials which are under study.

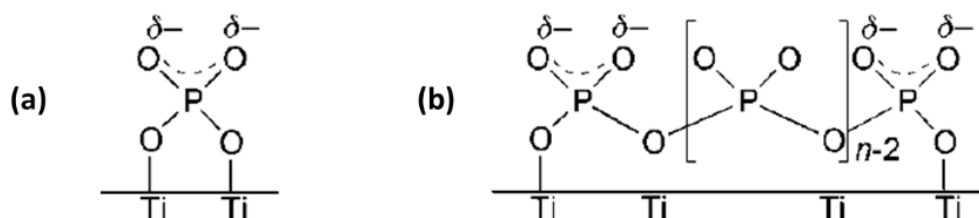


Figure 2.3 - Proposed bidentate binding confirmations for ortho (a) and poly (b) phosphate dispersants (Michelmore et al., 2003).

2.6 Alumina, silica and zirconia coating studies

The materials under study also contain coatings of alumina, silica and zirconia. Therefore, in this section we discuss some of the findings from the coating studies which have been reported in the literature to provide further insights towards the nature of the supplied materials and most importantly the nature of the inorganic coatings which have been applied to the surface of TiO_2 . The research which is discussed all employ the process of precipitating the inorganic coatings on suspensions of TiO_2 particles from acidic and basic solutions, for example for an alumina coated TiO_2 , solutions of aluminium sulphate and sodium hydroxide would be used. Usually one of these solutions is fed to a suspension of TiO_2 which is heated at a constant temperature and the rate at which the second solution is fed is controlled so that the pH of the heated suspension is maintained at a constant pH. Afterwards, the suspension is usually aged for 1 to 2 hours. In the literature, authors also refer to this aqueous precipitation coating procedure as the liquid deposition process.

The chemical mechanism for the deposition of alumina films on to the surface of TiO_2 via the aqueous liquid deposition process was investigated by Wu et al., 2006. Many researchers have also studied the influence of coating parameters on the structure of precipitated alumina (Wu, Wang, et al., 2006; Wu et al., 2007; Liu et al., 2009; Zhang et al., 2009; Dong et al., 2017; Dong et al., 2018), silica (Djerdjev et al., 2005; Liu et al., 2008; Veronovski et al., 2014; Xu et al., 2015; Dong et al., 2018), zirconia (Zhang, Yin, Wang, Liu, et al., (2010) and double-layers of silica and alumina (Zhang, Yin, Wang, Ren, et al., 2010; Li et al., 2012) on titanium dioxide. Since they are deposited in small concentrations and exhibit a thin layer, their characterisation precludes most techniques of structural analysis and their atomic structure therefore remains largely unknown (Kuznesof, 2010). Electron microscopy is therefore used to characterise coating morphologies, with elemental analysis techniques (i.e. ICP-AES, XRF, EDS, XPS) used to detect coating levels.

2.6.1 Alumina coatings

Using TEM, Wu, Wang et al. (2006) observed four different kinds of alumina coating morphologies when the coatings were precipitated from aluminium sulfate at different pH's and temperature's. Figure 2.4 displays the High Resolution TEM images of the different coating morphologies which were obtained. The coating morphology shown in Figure 2.4a was described as a dotted coating with nanoparticles adhered to the core particle surface, whilst the morphology displayed in Figure 2.4b exhibited a film coating with a uniform and continuous coating layer of several nanometres in thickness. The coating shown in Figure 2.4c and Figure 2.4d were described as floccule and flake coating respectively. Wu, Wang et al. (2006) also mapped out the conditions at which these different morphologies occurred. This morphology phase diagram is displayed in

Figure 2.5. In this figure, the temperature and pH refers to the temperature and pH at which TiO_2 particles were coated.

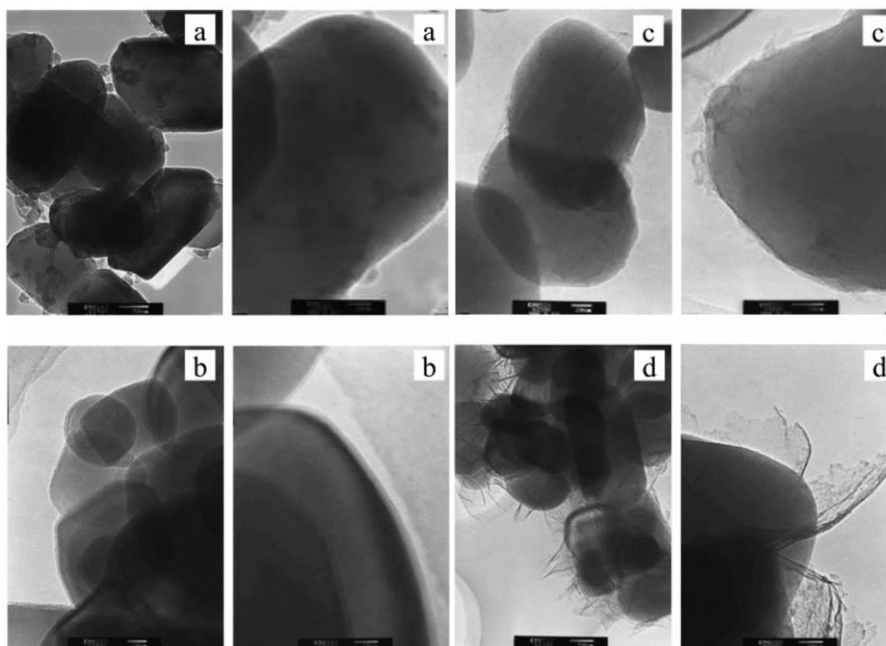


Figure 2.4 - The High resolution TEM images reported by Wu, Wang et al. (2006) for alumina coated TiO_2 . Dotted coating (a), film coating (b), floccule coating (c) and flake coating (d).

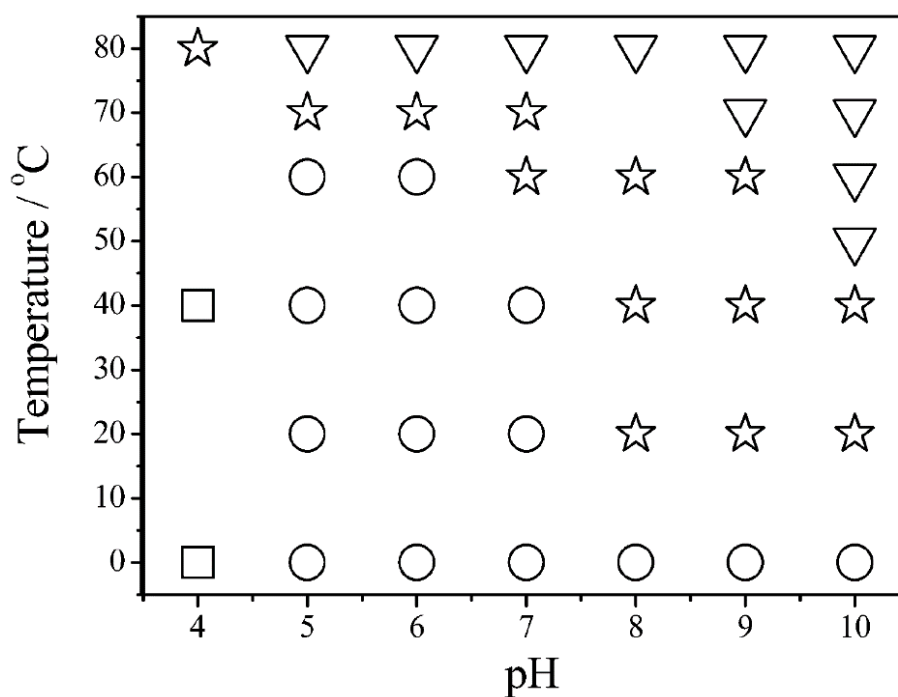


Figure 2.5 – The alumina morphology phase diagram produced by Wu, Wang, et al. (2006) as a function of temperature and pH. Dotted coating (squares), film coating (circles), floccule coating (stars) and flake coating (triangles).

In some works, the atomic structure of the alumina films have been inferred from the preparation and structural characterisation of hydrous alumina materials prepared under similar conditions (i.e. without any TiO_2 present) to the alumina coated TiO_2 (Wu et al., 2007; Dong et al., 2017). From these studies, three alumina phases were identified, amorphous alumina, pseudo-boehmite and bayerite. These works have also shown that a mixture of alumina phases can be present. The amorphous form of alumina lacks the long range structural atomic order required to be classified as a crystalline solid and is therefore described as the X-ray indifferent form as it does not produce defined peaks during XRD analysis. The pseudoboehmite form of alumina is a poorly crystallised form of alumina with a composition of $\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ where $2.0 > x > 1.0$ (Vieira Coelho et al., 2008). Its X-ray diffraction pattern displays broad bands which coincide with the strong reflections of the well crystallised aluminium oxide hydroxide boehmite (Hudson et al., 2012). The crystal structure consists of octahedral layers in the xz plane and a single or very few octahedral layers in the y plane. Between these layers, water is intercalated (Tettenhorst, Rodney et al., 1980). In fact, as much as 30.7% of pseudoboehmite can be water (Baker and Pearson, 1974). In contrast to amorphous alumina and pseudoboehmite, bayerite (an aluminium tri-hydroxide) is a well-defined crystalline solid (Misra, 2003; Hudson et al., 2012) which exhibits long range atomic order.

2.6.2 Silica coatings

The effects of coating parameters on the film morphologies of silica coatings has also been investigated. Liu et al. (2008) found that the silica films could exhibit two types of film morphology. Formed silica coatings were prepared from sodium silicate using various sodium silicate loadings, pH's and temperatures. Two types of morphologies were observed. Examples of the two types of silica morphologies formed on TiO_2 particles are displayed in Figure 2.6. The film morphology displayed in Figure 2.6a was found to be composed of silica nanoparticles with an average size of 15 nm. The average thickness of the resultant island like coating layers were also found to be approximately 8 nm. This type of coating was formed at a pH of 7 to 9. The 2nd type of morphology observed featured a dense continuous and uniform film with island like coating layers. The average thickness of this coating was reported to be 5 nm and the island-like coating layers were formed with an average particle size of 13 nm. This morphology type was formed when the pH had been increased to 9.5. Similar types of silica coating morphologies were also observed and reported by Xu et al. (2015) who investigated the influence of different injection methods (different ways of transferring the solutions of Na_2SiO_3 and H_2SO_4 into the TiO_2 suspension) on formed silica coating layers. The silica coatings were prepared at a pH of 9.3 – 9.5 and a temperature of 85°C. The silica film morphology shown in Figure 2.7a was found to display a flocculent and discontinuous layer composed of silica nanoparticles. This film morphology was formed by successive injection of Na_2SiO_3 and then H_2SO_4 . The silica

morphology displayed in Figure 2.7b was found to display a continuous and compact silica coating layer and was formed by simultaneous injection of Na_2SiO_3 and H_2SO_4 . Liu et al. (2008) also showed that the silica coating layers were anchored at the surface of TiO_2 via Ti–O–Si bonds and postulated that the silica coating existed as an amorphous phase.

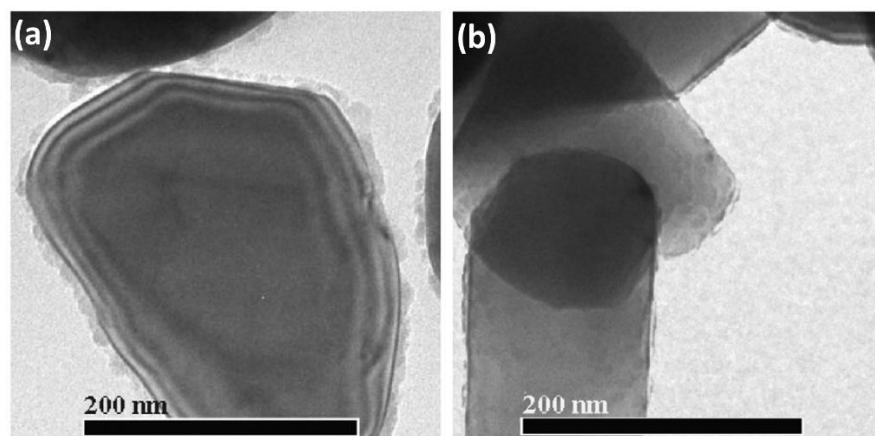


Figure 2.6 - Examples of TEM images of silica coated TiO_2 . Silica coated TiO_2 samples were formed at a temperature of 90°C at (a) pH 7 and (b) pH 9.5 (Liu et al., 2008).

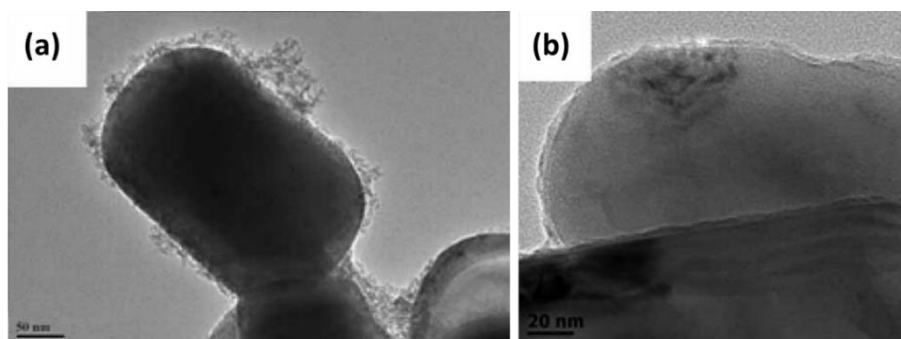


Figure 2.7 - TEM images obtained by Xu et al. (2015) when two different injection methods were used to obtain silica coated TiO_2 . (a) Successive injection and (b) simultaneous injection.

2.6.3 Zirconia coatings

Zhang, Yin, Wang, Liu, et al. (2010) investigated the liquid deposition of zirconia onto the surface of TiO_2 particles and found that two types of film morphologies were formed when coating parameters such as pH and the zirconia loading were varied. The zirconia coatings were prepared at a temperature of 80°C from a solutions of ZrOCl_2 and NaOH . Examples of the two types of morphologies observed by Zhang, Yin, Wang, Liu, et al. (2010) are displayed in Figure 2.8. The zirconia film morphology shown in Figure 2.8a was found to exhibit a continuous and thin

zirconia coating layer and was found to form when the pH of the reaction solution was 7. This coating was also found to be composed of small sized zirconia nanoparticles with an average particle size of 3 nm. The 2nd film morphology formed shown in Figure 2.8b was found to feature a continuous and dense zirconia coating layer. These zirconia coating layers were found to be composed of small sized zirconia nanoparticles with an average particle size of 4 nm and was formed when the pH of the solution was greater than 7. Higher pH's were thought to promote the rapid hydrolysis of ZrOCl_2 and the growth of the zirconia nanoparticles, which were formed by homogeneous nucleation rather than heterogeneous nucleation. The influence of zirconia loading was also investigated with mole ratios of ZrOCl_2 to TiO_2 of 1:153 to 1:30, and with increasing zirconia loadings, the thickness of the zirconia coating layers were found to become thicker, whilst at lower zirconia loadings, the TiO_2 surface was found to be not completely covered by the zirconia coating layer. With increasing zirconia loadings, larger sized zirconia aggregates were also formed on the zirconia coating layers.

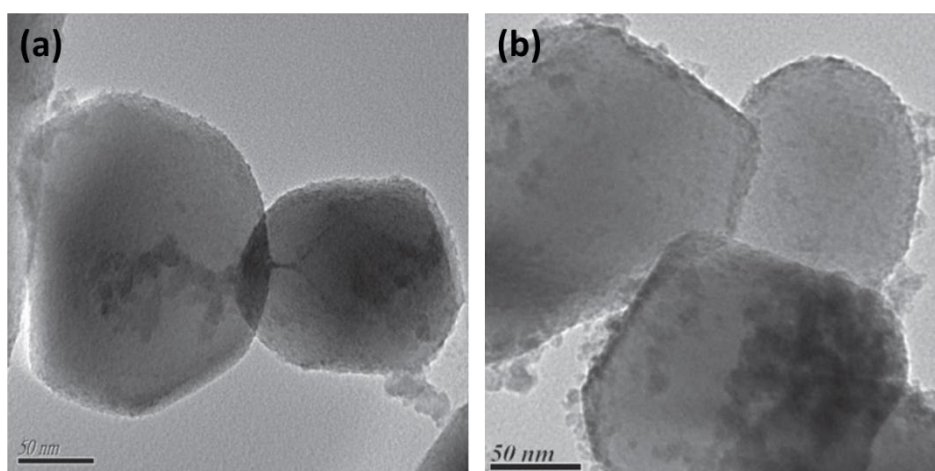


Figure 2.8 - TEM images of zirconia coated TiO_2 . (a) Continuous and thin coating layer and (b) continuous and dense coating layer (Zhang, Yin, Wang, Liu, et al., 2010).

2.6.4 Alumina-silica coatings

Zhang, Yin, Wang, Ren, et al. (2010) prepared double layer coatings of alumina/silica on TiO_2 . The alumina/silica phases were amorphous and were formed at the surface of TiO_2 particles using sodium silicate and sodium aluminate. The morphologies of the double layer coatings featured continuous and uniform coating layers (Figure 2.9) and were anchored at the surfaces of rutile TiO_2 via Si–O–Ti bonds. Alumina coating layers were also probably anchored at the surfaces of the silica coated TiO_2 via Al–O–Si bonds. The thickness of the binary alumina/silica coating layers were also found to increase with the increase in the mole ratios of NaAlO_2 to TiO_2 . Double

layer coatings of alumina/silica on TiO_2 were also prepared by Li et al. (2012) using sodium silicate and aluminium sulfate. The precipitated alumina films were found to exhibit two types of morphologies (Figure 2.10). The first alumina morphology featured a compact and continuous film and was obtained at pH 4 and a temperature of 60°C. The 2nd morphology displayed a loose and flocculent film and was obtained at pH 8.5 and a temperature of 60°C.

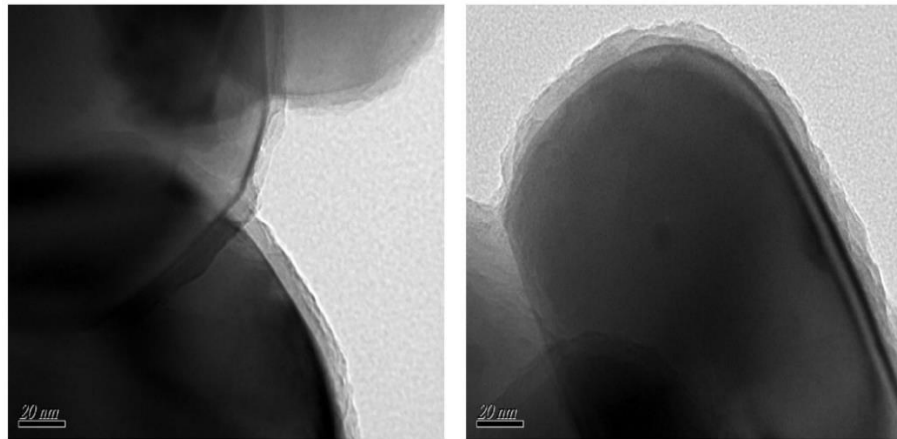


Figure 2.9 - Examples of TEM images obtained by Zhang, Yin, Wang, Ren, et al. (2010) for binary alumina/silica coated TiO_2 .

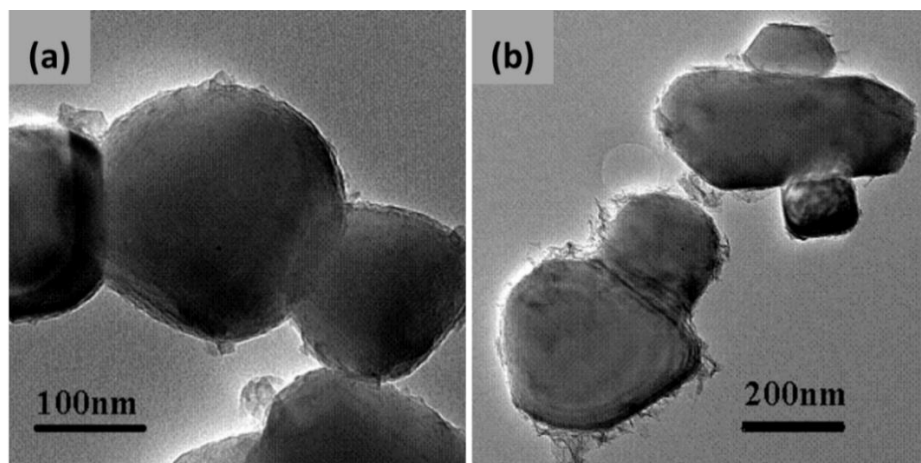


Figure 2.10 – Alumina/silica double layer coated TiO_2 prepared by Li et al. (2012).

2.6.5 Influence of dispersant on coating morphology

As well as coating conditions, Dong et al. (2018) also showed that the dispersant type could influence formed alumina and silica film morphologies. Silica and alumina coated rutile samples were prepared with four different pre-dispersants. Sodium silicate nonahydrate (SSNH), sodium

hexametaphosphate (SHP), sodium dodecylbenzene sulfonate (SDBS) and polyethyleneglycol 1000 (PEG) were selected as pre-dispersants. The formed alumina and silica film morphologies obtained with different pre-dispersants are displayed in Figure 2.11. When SSNH was used, rutile TiO_2 samples were successfully coated with a continuous layer and compact hydrous silica film. With SHP, a discontinuous flocculent hydrous silica layer was detected and with SDBS and PEG pre-dispersants, samples were coated with relatively compact and continuous silica films. When no pre-dispersant was utilised, the hydrous silica films were found to display discontinuous and flocculent silica film. When hydrous alumina was deposited on rutile TiO_2 with SSNH pre-dispersant, the alumina film was found to exhibit a reticular structure. With SHP, the surface of TiO_2 particles displayed hydrous alumina agglomerations. A flocculent hydrous alumina film was obtained with SDBS pre-dispersant, whilst a hydrous alumina film with a slight flocculent and fibrous structure was formed when PEG pre-dispersant was employed. When no pre-dispersant was used, hydrous alumina was deposited and agglomerated onto the surface of rutile TiO_2 . Therefore, it appeared that SHP had little influence on formed silica and alumina film morphologies. Dong et al. (2018) also concluded that the morphologies of the formed silica and alumina films were mainly influenced by the functional groups of the pre-dispersants rather than the dispersion stability of the rutile TiO_2 suspensions.

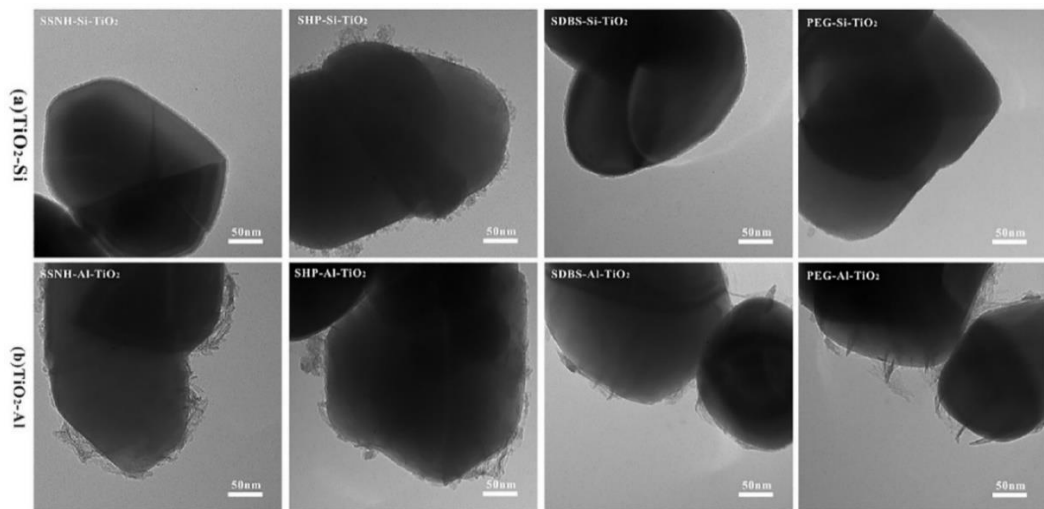


Figure 2.11 - TEM images of formed hydrous silica and alumina films obtained with pre-dispersants of sodium silicate nonahydrate (SSNH), sodium hexametaphosphate (SHP), sodium dodecylbenzene sulfonate (SDBS) and polyethylene glycol 1000 (PEG) (Dong et al., 2018).

2.6.6 Influence of coatings on specific surface area and suspension rheology

When coated with alumina the surface area of the titanium dioxide has been found to increase significantly. According to Braun et al. (1992), the calculated specific surface area of $0.2 \mu\text{m}$

spheres is 7 m²/g, which is consistent with reported literature values of 6 – 8 m²/g (Day and Egerton, 1987; Johansson and Losoi, 1991; Veronovski et al., 2014). Since precipitated alumina has a surface area of 200 m²/g, each per cent of alumina precipitated onto the surface of TiO₂ adds approximately 2 m²/g of surface area (Braun et al., 1992), which therefore serves as a general rule/guide. Typical surface area values reported for 2.7 – 3.0% alumina coated TiO₂ are 15.8 – 30 m²/g (Day and Egerton, 1987; Johansson and Losoi, 1991; Siwińska-Stefańska et al., 2008) and as much as 35.0 m²/g has been reported for coating levels of 4.7% (Siwińska-Stefańska et al., 2008). These authors gave no indication as to whether the reported surface areas were linked to a specific alumina phase or morphology.

The surface coatings have also been shown to influence suspension rheology. Li (2019) showed that the suspension viscosity is decreased when the surface of TiO₂ dosed with sodium polyphosphate dispersant was coated with 3 wt% hydrous alumina. Furthermore, rheological analysis was undertaken by Morris et al. (1999) on unmodified, alumina and silica coated pigments. At the iso-electric point, the suspension yield stress was found to decrease with increasing numbers of aluminium and silicon hydroxide groups at the pigment surface. Since the Hamaker constants of the three pigment components; rutile, alumina and silica in water (A_{131}) are 6.0×10^{-20} , 2.75×10^{-20} , and 0.16×10^{-20} J respectively, the reduction of the yield stress was attributed to the reduction of the composite Hamaker constant, i.e. a surface composed of TiO₂ and alumina or TiO₂ and silica.

2.6.7 Coating summary and potential implications for this research

Inorganic coatings such as alumina, silica and zirconia precipitated onto the surface of TiO₂ have various morphologies and these coatings influence the surface texture of the TiO₂ surface. The morphologies of these formed coatings are highly dependent upon the parameters of the coating procedure, i.e. coating temperature and pH. These coating parameters are also thought to influence the structural phase of the inorganic coating. The morphologies of the coatings have also been found to be influenced by the type of dispersant present. However, for alumina and silica coatings, if sodium polyphosphate is present, this dispersant type has no effect on the formed coating morphology. These inorganic coatings have also been found to influence properties such as specific surface area and suspension rheology.

In light of these findings, for this research, these studies have raised certain questions. Firstly, due to the fact that the inorganic coatings can display a range of morphologies and influence the surface texture / surface roughness of the TiO₂, it is not known to what effect that these coatings may influence the contact area between spray dried / spin flash dried granules. This is because a change in contact area can affect interparticle cohesion strength and therefore powder rheology. Furthermore, these coatings also change the surface composition of the TiO₂. For this research, it

is not known to what degree a change in the surface chemistry may influence interparticle cohesion. In a similar way to suspension rheology, these coatings may also influence powder rheology

2.6 Spray drying of TiO₂

To the best of our knowledge, only one academic work has investigated the spray drying of TiO₂ pigment (Li, 2019) and our review of the literature could not find anything related to the spin flash drying of TiO₂ or spin flash dried TiO₂. In fact, published works related to spin flash drying and spin flash dried powders of any kind were extremely scarce. With regards to spray drying and spray dried powders, substantial academic literature has been reported. Despite the operation principles of spray drying and spin flash drying differing, the removal of water from a dispersion via agitation and then drying is likely to share similarities in both drying operations. Therefore, the following discussions of spray drying TiO₂ is likely to be relevant to the study of spin flash drying and spin flash dried TiO₂ powders.

Li (2019) investigated the spray drying of unmodified TiO₂ and 3 wt% alumina surface treated TiO₂. The spray drier feed slurries for both materials were formulated at the iso-electric point (flocculated system) and at distance from the iso-electric point (dispersed system). For the spray drying of alumina surface treated TiO₂, different granule morphologies were observed for the drying of a dispersed system in comparison to a flocculated slurry (Figure 2.12). The drying of a flocculated slurry produced granules with spherical morphologies (Figure 2.12a), whilst the drying of a dispersed slurry produced granules with buckled structures (Figure 2.12c). For the spray drying of unmodified TiO₂, regardless of whether the system was dispersed or flocculated, the granules formed exhibited spherical morphologies similar to those shown in Figure 2.12a. The internal structures of spray dried granules were also investigated using Scanning Electron Microscopy (SEM), microtome sectioning and Focussed Ion Beam (FIB) SEM techniques. Regardless of the type of TiO₂ spray dried, unmodified or alumina surface treated, all spray dried granules were found to display solid internal structures. Shown in Figure 2.12b and Figure 2.12d are examples of spray dried alumina surface treated TiO₂ granules displaying solid internal structures.

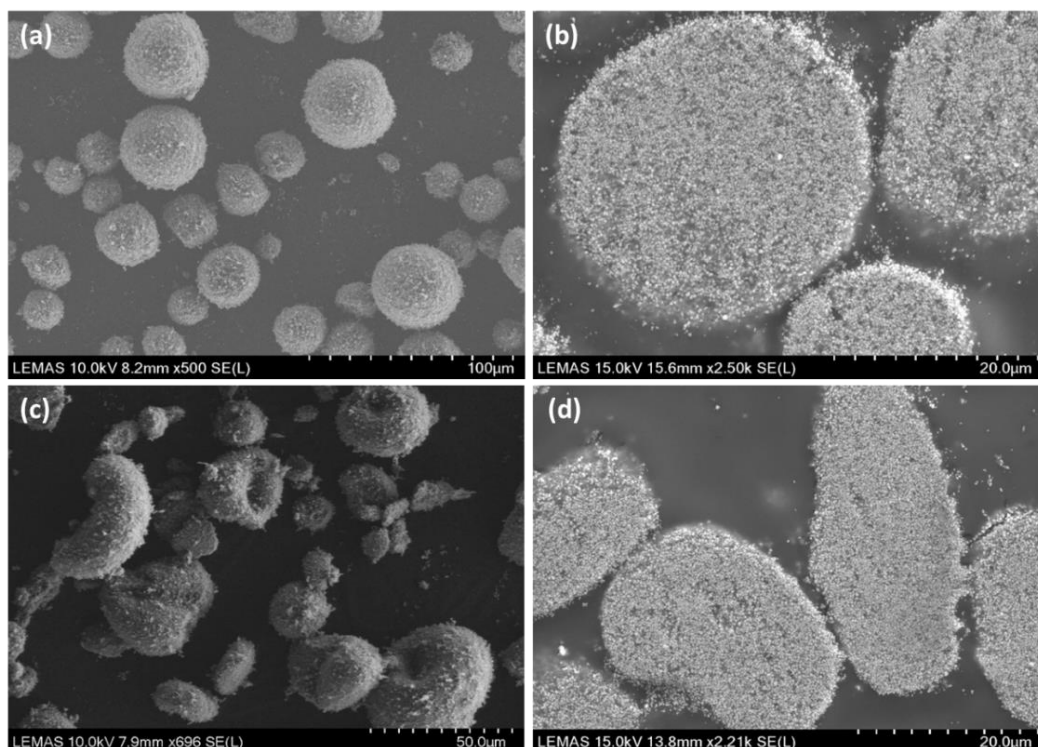


Figure 2.12 - Typical images obtained by Li (2019) during the spray drying of alumina coated titanium dioxide (a) spherical granules, (b) microtome cross sections of spherical granules (c) buckled granule structures and (d) microtome cross sections of buckled granules.

In the drying of ceramic systems, a number of studies have shown that the drying of flocculated slurries produce granules with spherical morphologies, whilst the drying of a dispersed slurry results in granules with buckled structures or morphologies which deviate from spherical structures (Takahashi et al., 1995; Jr. Walker et al., 1999; Tsubaki et al., 2002; Bertrand et al., 2003; Filiatre et al., 2003; Roy et al., 2005; Zainuddin et al., 2010; Naglieri et al., 2013). Therefore, the results obtained by Li (2019) for the drying of alumina surface treated TiO_2 were consistent with the findings of others. The driving force for droplet buckling during drying has been quantitatively analysed by Lintingre et al. (2016), who has shown that the capillary pressure is the main driving force for buckling.

When drying a flocculated system the open porous network keeps the capillary pressure low. In contrast, during the drying of a dispersed system, particle mobility is high and the primary particles within the droplet accumulate at the surface of the droplet. This accumulation occurs because the evaporative removal of water from the droplet is much higher than the rate at which the primary particles are able to diffuse and redistribute themselves due to Brownian motion. Consequently, a shell is formed with a low porosity around the droplet which leads to the

development of high capillary pressure. Further moisture removal and drying leads to buckling and the final granule structure which is formed exhibits a buckled or non-spherical morphology.

In the work of Li (2019), single droplet drying studies were also undertaken with unmodified TiO_2 and alumina surface treated TiO_2 , formulated at the iep and at distance from the iep. The results obtained were found to be consistent with the quantitative analysis of Lintingre et al. (2016), i.e, spherical granules morphologies are formed with the drying of flocculated slurries, whilst the drying of a dispersed slurry produces buckled granule structures. As there was a discrepancy between the spray drying and single droplet drying results in the work of Li (2019), the drying of dispersed systems of unmodified TiO_2 and alumina surface treated TiO_2 was investigated further. The influence of droplet size was considered. This is because droplet size in single droplet drying experiments are usually much larger than the droplets atomised in “real” spray driers. Therefore, single droplet drying experiments were undertaken with droplet sizes of 0.4 – 2.5 μL . The buckling behaviour of alumina surface treated TiO_2 was found to be independent of droplet size. These results contrasted with single droplet drying of dispersed unmodified TiO_2 , which was found to be dependent on droplet size. Larger droplet sizes produced the expected buckled structures, whilst the smaller droplets formed spherical structures which deviated from expected trends. These results suggested there was a resistance to the formation of a shell (which is critical for buckling to occur) in drying of smaller sized droplets and was attributed to the dispersing effect of the polyphosphate dispersants. The polyphosphate dispersants are anchored to the surface of unmodified TiO_2 and whilst these dispersants are still present in the alumina surface treated TiO_2 , it is possible that these dispersants are coated by the alumina. Therefore, in smaller droplets, the presence of the polyphosphate dispersants anchored at the surface of unmodified TiO_2 provided increased particle mobility preventing the formation of a solid shell and the occurrence of buckling.

2.7 Conclusions

To achieve optimum performance for specific applications, different grades of TiO_2 are required. TiO_2 grades can differ by the crystalline phase of the primary TiO_2 particle, doping of the crystalline TiO_2 , the primary particle/crystallite size and the composition and morphology of the subsequent coating(s). Furthermore, due to the requirements of different grades, the bulk handling behaviour of the pigment can also differ and this can create challenges between manufacturing and producing the required grade for a specific application.

Pigment TiO_2 is produced by either the sulfate or chloride process and afterwards the pigment undergoes a finishing process to modify the surface of TiO_2 for the required application. The TiO_2 particles start life as highly agglomerated crystallites, which are subsequently slurried in water

and wet milled to reduce their size. During this process, dispersants such as sodium hexametaphosphate are absorbed and chemically bonded to the surface. The milling process breaks down the agglomerated crystallites into 1 μm sized aggregates. The work of Austin et al. (2021) also suggests that the aluminium dopants reside under the surface of the TiO_2 and during the milling process become increasingly exposed. However, a discrepancy still remains in the literature regarding the location of the aluminium within the TiO_2 crystallite. Some authors claim that the dopants reside to a greater degree at the surface, whereas others suggest it lies within the bulk of the pigment. After the milling process, the surface of the TiO_2 is surface treated with hydrous metal oxides and hydroxides. The most common surface treatment applied is alumina. The morphologies of the formed surface films are highly dependent on the deposited metal oxide/hydroxide and the conditions employed during its deposition. After coating, the pigment is washed to remove unwanted salts and then dried. To dry the pigment, drying techniques such as spray drying and spin flash drying can be used. During these processes, the coated wet slurry is atomised into droplets and the coated aggregates are assembled into granules. In terms of spray drying, the shapes of the granules are highly dependent on the slurry pH / slurry stability. Spherical granules are typically formed when the slurry is adjusted to the iso-electric point, whereas buckled structures are formed when the slurry is adjusted away from the iso-electric point. However, for uncoated grades, the work of Li (2019) suggests that the slurry pH has little effect and spherical granules are produced regardless. The spray dried titanium dioxide granules are also known to feature solid throughout constructions. Displayed in Figure 2.13 is an illustration displaying the evolution of the pigment as it travels through the coating process. For this research, this illustration also essentially summarises the most important aspects of the coating process for the production of titanium dioxide pigment.

For the bulk handling behaviour of spray dried and spin flash dried titanium dioxide, this literature review has raised several questions. Throughout the coating process, the surface chemistry of the TiO_2 varies due to the presence of the aluminium dopant and the degree of milling, the presence of polyphosphate dispersants and the presence of coatings such as alumina, silica and zirconia. Rheological studies have shown that the surface chemistry influences the slurry rheology and this is also likely to be the case for powder flow and powder cohesion. Moreover, a range of morphologies can result from the precipitated hydroxides, which is likely to produce varying degrees of surface roughness and it is not known how these morphologies are likely to influence powder cohesion and bulk powder flow. For the supplied samples, it is also not known what shapes and structures the granules are likely to exhibit. This is because the spray dried granule shape and structure has been shown to be highly dependent on the slurry pH / stability. Granule shape and structure is also likely to have important implications for powder flow and breakage respectively.

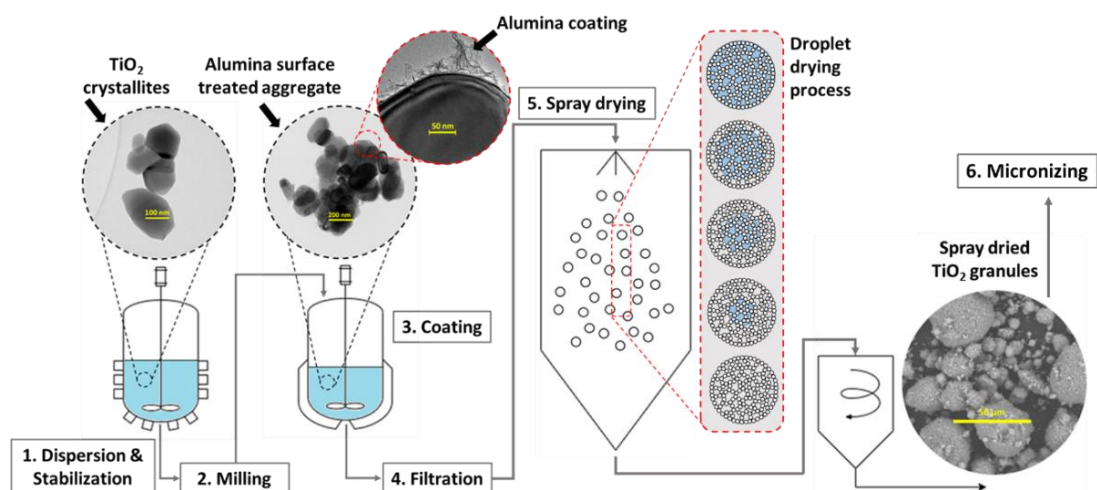


Figure 2.13 - A pictorial representation of the coating process displaying the evolution of the TiO₂ pigment as it travels through the coating process.

Chapter 3 – Powder characteristics

3.1 Introduction

The bulk handling behaviour of particulate solids arises from the forces acting on them, i.e. the gravitational force, the frictional contact forces and the attractive forces between particles. Particle characteristics such as size and shape can control the distribution of these different forces and ultimately the bulk handling behaviour of the particulate solid. For example, powder flowability is known to drastically reduce for particles with sizes less than tens of microns (Hassanpour et al., 2019). Therefore, for a new particulate system, the powder characteristics must be fully quantified to understand the powders bulk handling behaviour. Thus, the main aim of this chapter has been to develop an initial understanding of the powder characteristics for subsequent chapters. Characteristics of interest included particle size, size distribution, particle shape/morphology, in addition to moisture sorption as a function of the relative humidity and specific surface area.

Particle size is probably the most important property which needs to be characterised for understanding the bulk handling characteristics of a powder, such as powder flowability as it will determine whether the gravitational forces or interparticle cohesive forces such as van der Waals are dominant. Generally, the competition between these two types of forces are discussed in terms of the bond number, Bo (Equation 3.1);

$$Bo = \frac{f_{int}}{mg} \quad (3.1)$$

where f_{int} is the interparticle force and mg is the gravitational force (Hassanpour et al., 2019). When the gravitational force is greater than the interparticle forces, Bo is <1 , and the powder is termed as being non-cohesive. In contrast, when the interparticle forces are greater than the gravitational forces, Bo is >1 , and the powder is categorised as being cohesive. Usually for particulates with a size below 100 μm , the interparticle forces become increasingly substantial. This is because the magnitude of the interparticle forces are proportional to the particle diameter, whereas the gravitational force is proportional to the particle diameter cubed (Hassanpour et al., 2019). A reduction in size also increases the number of contacts between particles, which therefore increases cohesion (Ganesan et al., 2008). Therefore, for particles with a size less than tens of microns, a greater cohesive behaviour can reduce the possibility of gravitational flow or even gas fluidisation. In comparison, when the particles are large over a fraction of a millimetre, the flowability is usually good, especially when the particles are reasonably round.

Powders rarely exist as monodispersed systems and instead a distribution of sizes will exist. A theoretical monodispersed particulate system has a maximum packing fraction of 0.64. When the

distribution widens, the maximum packing fraction and particle coordination number increases. This is because the smaller particles enter the voids between the larger particulates. Thus, a tightly packed structure is formed which is less able to flow. Therefore, the finer the particle size and the greater the range of particle sizes, the greater the cohesive strength, and the lower the powder flow rate is likely to be (Ganesan et al., 2008).

Particle shape is also important since it can control the magnitude and orientation of the contact forces. In a dense flow of particulate solids, a non-spherical shape can prevent particle rotations affecting the powder rheology in comparison to a system of spherical particulates. An irregular particle shape can also lead to an increase in interparticle friction since irregular shaped particles have the ability to interlock affecting bulk characteristics such as packing and flow. For example, particles which are more spherical are known to pack better than irregular shaped particles (Abdullah and Geldart, 1999). Moreover, particle shapes such as platelets, fibres, or needles encourage mechanical interlocking, allowing large arches to form and preventing flow at outlets (Hassanpour et al., 2019). Spray dried granules are also known to exhibit a range of morphologies/shapes, such as spherical or buckled structures (Walton, 2000). Therefore, shape analysis is especially important for this study.

The moisture content of a powder can also influence bulk powder handling through the formation of liquid bridges/menisci between particles (Shah et al., 2017). These attractive capillary forces form between particles when they are in close proximity and the powder absorbs water vapour at its surfaces. Eventually a liquid phase builds up and capillary menisci form between the particles creating an attractive force (Tselishchev and Val'tsifer, 2003). Specifically, to titanium dioxide powders, it is known that pigments with higher levels of coatings show greater levels of moisture sorption (Day, 1990), but it has not been explicitly stated as to why.

The moisture content of a powder will also be dependent on the environmental relative humidity since an equilibrium between the air moisture and particle surface moisture content will exist. Therefore, understanding the moisture sorption characteristics of a powder as a function of the relative humidity can therefore provide valuable insights for predicting whether powder moisture content is likely to have an impact on powder flow behaviour. This is because when the moisture content of a powder increases, the cohesiveness of the powder generally increases (Ganesan et al., 2008), and furthermore, as the relative humidity increases, the moisture content of a powder also tends to increase.

To investigate the particulate characteristics for the supplied materials, scanning electron microscopy (SEM), laser diffraction (LD), automated static image analysis (ASIA) and dynamic vapour sorption (DVS) techniques have been employed. In subsequent chapters, the data reported

in this chapter is then used to understand the bulk handling behaviours of the materials under study.

In this work, SEM was utilised to quickly image spray dried and spin flash dried titanium dioxide granules for their general size and shape, but also to image their surface characteristics such as crystallite size and to identify the presence of the surface coatings. The use of SEM for particle characterisation requires no further introduction or mention.

To determine the average particle size and evaluate particle size distributions, two techniques utilising different measurement principles have been employed, LD and ASIA. Due to their working principles and their advantages and disadvantages, these two techniques have provided complementary data for accurately assessing the size of spray dried and spin flash dried titanium dioxide. LD was undertaken using a Malvern Mastersizer 2000 equipped with a Scirocco dry feeder unit. The advantage of using this setup includes its speedy data acquisition time, which is typically less than a couple of minutes and its ability to sample sufficient quantities of powder. LD also has a broad particle size range, which means both the coarse and fine fraction of particles in a given sample can be measured (Ottewell, 2015). However, the dynamic measurement principles of laser diffraction can lead to poor particle sizing results if breakage or auto agglomeration occurs during dispersion and during transport of the sample to the detector using the Scirocco dry feeder unit. Spray-dried powders are particularly prone to attrition because of their porous and weak structure (Bonakdar, 2016) and furthermore, auto-agglomerates readily form when the particle size falls below 20 μm (Ottewell, 2015). Therefore, for this study, the influence of breakage and auto-agglomeration was carefully considered during particle size analysis. With its imaging capability, ASIA was undertaken using a Malvern Morphologi G3, and the obvious advantage of this setup was its ability to image every single particle which had been dispersed onto a glass slide (Ottewell, 2015). The obtained images from this image analysis could then be quickly examined to check for breakage and auto-agglomerates. However, the disadvantages of this technique can include its long data acquisition time and small measured sample volume. Therefore, the data obtained from both techniques were found to be complementary allowing a proper particle size assessment for the supplied materials. Moreover, the Malvern Morphologi G3 also provided the required shape analysis needed for this work.

Powder moisture sorption as function of the relative humidity was evaluated using DVS with water as a probe molecule, and furthermore, vapour sorption experiments with nitrogen as a probe molecule allowed the surface area of the supplied materials to be determined. For this work, information on the surface area's was important for identifying the presence of coatings/surface treatments, since it is known that the surface area of surface treated titanium dioxide increases

substantially with the addition of alumina coatings (Day, 1974; Day and Egerton, 1987; Zhang et al., 2015; Auer et al., 2017; Li, 2019).

3.2 Materials and methods

3.2.1 Materials

Sampled from industrial driers, granulated titanium dioxide powders were supplied by Venator Materials PLC. It must also be noted here, that the supplied powders are actually intermediates which are utilised to produce TiO₂ pigment products. The granulated materials were prepared from dispersions of aluminium doped rutile titanium dioxide containing inorganic coatings of alumina (Al₂O₃) and/or silica (SiO₂) and zirconia (ZrO₂). Before drying, the inorganic coatings were applied to the surface of titanium dioxide aggregates by precipitation and deposition of the oxide onto the surface of titanium dioxide aggregates in aqueous solutions. Before drying, the dispersions were also formulated to solids concentrations of ~40 wt% and a pH value between 6 - 8.

The four granulated TiO₂ powders differed by the dispersions in which each powder was prepared from. Specifically, by the titanium dioxide crystallite size, the type of inorganic coatings applied to the aggregates in the dispersion and by the level/thickness of this coating. During processing, these powders have also displayed significant differences in their powder handling behaviour.

The first sample was a spray dried powder prepared from a rutile titanium dioxide dispersion featuring 0.5 wt% alumina coating. Throughout this work, this sample will be known as SD0.5.

The second sample was prepared from a dispersion of rutile titanium dioxide aggregates coated with 3.0 wt% alumina. This dispersion had also been spray dried. Throughout this work, this sample will be referred to as SD3.0.

The third sample featured spray dried granules which had been prepared from a dispersion containing rutile titanium dioxide aggregates coated with an initial 0.5 wt% silica surface treatment and a final outer coating of 3 wt% alumina. Throughout this work, this sample will be referred to as SD3.5.

A fourth powder sample was prepared from a dispersion of rutile titanium dioxide aggregates coated with 0.5 wt% zirconia and a 2nd final outer coating of 3 wt% alumina. This dispersion was then spin flash dried. Throughout this work, this sample will be referred to as SFD3.5.

The formulations and drying methods used to prepare each powder are summarised in Table 3.1.

Table 3.1 – A summary of the formulations and drying methods used to prepare each powder.

Sample	TiO₂ crystallite size (nm)*	1st coating (wt%)	2nd coating (wt%)	Drying method
SD0.5	266	0.5 (Al ₂ O ₃)	-	Spray drying
SD3.0	297	3.0 (Al ₂ O ₃)	-	Spray drying
SD3.5	297	0.5 (SiO ₂)	3.0 (Al ₂ O ₃)	Spray drying
SFD3.5	315	0.5 (ZrO ₂)	3.0 (Al ₂ O ₃)	Spin flash drying

*Note: TiO₂ crystallite size was determined by image analysis of SEM images. The complete particle size analysis can be found reported in the appendix. The crystallite size listed in Table 3.1 is reported as the D[v,50].

Before any analysis on the supplied powders were undertaken, the powders were dried in an oven at 50-60°C to remove excess moisture which may have accumulated. After drying, each powder was then passed through a 500 µm sieve to removed excessively large particle agglomerates, for example spray drier wall debris. The influence of removing material >500 µm was investigated by sizing the as supplied powder and comparing it against material <500 µm. The data for this analysis can be found in the supplementary data section in Figure A3.1. After sieving, each powder was studied using the following techniques. During this analysis, the lab temperature was recorded at ~22°C and the relative humidity was found to vary between 20-40 %.

3.2.2 Scanning electron microscopy

To image the samples, two types of Scanning Electron Microscopes (SEM) were used depending on the analysis requirements. To image multiple granules, an Hitachi TM3030Plus desktop SEM equipped with SE (secondary electron) and BSE (back scattered electron) detectors was used. To image single granules and the surface of spray dried granules, an Hitachi SU8230 Cold Field Emission (CFE) Scanning Electron Microscope (Oxford Instruments) was used as this instrument was capable of producing the required magnification.

To prepare samples for use with the Hitachi TM3030Plus desktop SEM, samples were deposited on to a carbon film attached to an aluminium sample stub and excess sample was removed by using lightly sprayed compressed air.

To prepare samples for the Hitachi SU8230 Cold Field Emission (CFE) SEM, samples were prepared the same as for the Hitachi TM3030Plus desktop SEM, however these samples were also coated with approximately 10 nm of iridium.

3.2.3 Laser diffraction

Particle size distributions were also measured using a Malvern Mastersizer 2000E equipped with the Scirroco dry feeder dispersion unit. The dry feeder unit was set to a pressure of 0 bar and the powder samples were fed into the unit via a vibrating chute. After leaving the chute, the powder

samples fell under gravity into the sample inlet port. Afterwards, the granules impact at the 90° bend of the Scirroco dispersion unit, which is thought to disperse the sample for size measurement. The powder sample is then subsequently pulled through the sample measurement cell via a vacuum system.

During measurement of the particle size distributions, the Mastersizer undertook 5 measurements which were then automatically averaged by the systems software in order to provide a single result. In order to check reproducibility, measurements were made in duplicate and a single result was reported. The obscuration was controlled at 3.3 ± 0.8 % and the following material constants were used for Rutile TiO₂: Refractive index = 2.741, absorption = 0.1.

3.2.4 Automated static image analysis

To investigate particle size and shape, automated static image analysis was employed using a Malvern Morphologi G3 (Malvern Instruments, Worcestershire, UK) instrument. Using the instruments automated dispersion unit and a low dispersive energy (1.0 bar injection pressure, 20 ms injection time and 60 s settling time), 5 mm³ of powder sample was dispersed onto a glass slide in order to form a monolayer of particles. A 5 megapixel camera with a 5x (6.5 – 420 µm) objective lens was then used to image 200,000 particles.

3.2.5 Dynamic vapour sorption

The moisture sorption characteristics of spray dried and spin flash dried titanium dioxide powders were investigated using Dynamic Vapour Sorption (DVS Advantage Surface Measurement Systems, Middlesex, UK) with water as an absorbate. Samples were loaded into a sample pan and an empty pan was used as a reference. At a constant temperature of 25°C, the relative humidity (RH) was increased from 0 to 90% at increments of 10% RH. At each RH step, the sample was allowed to reach a gravimetric equilibrium. When the change in mass (dm/dt) was lower than 0.002 mg/min, the sample was then allowed to progress to the next RH step.

3.2.6 Specific surface area

Specific surface area measurements were undertaken with nitrogen gas at 77 K using a surface analyzer (TriStar 3000, Micromeritics, US). Prior to analysis a free space measurement was carried out using helium. The system was then evacuated and full nitrogen adsorption isotherms were undertaken.

TiO₂ samples were degassed using a Micrometric FlowPrep 060 under a flow of nitrogen and by heating to 230°C for a minimum of 3 hours before cooling and weighing to obtain the dry sample masses.

3.3 Results and discussion

3.3.1 Microscopic observations

The supplied materials were first imaged using SEM and shown in Figure 3.1 are typical images obtained for each sample. On initial examination of these images, the spray dried granules (Figure 3.1a, 3.1b and 3.1c) were found to be reasonably spherical with a broad size distribution. The spin flash dried granules (Figure 3.1d) also exhibited a broad size distribution, however the granules exhibited a non-spherical and irregular shapes. In all images, fine particles can also be seen adhered to granule surfaces. The presence of capillary menisci were not detected in these images and all powders appeared relatively dry. Typical single granules were also imaged at a higher 5000x magnification. These images are displayed in Figure 3.2. For each sample type, these images clearly display structures assembled from TiO_2 aggregates. Consistent with previous SEM images displayed in Figure 3.1, these micrographs also further emphasize the spherical nature of spray dried granules and the irregular shapes of spin flash dried granules.

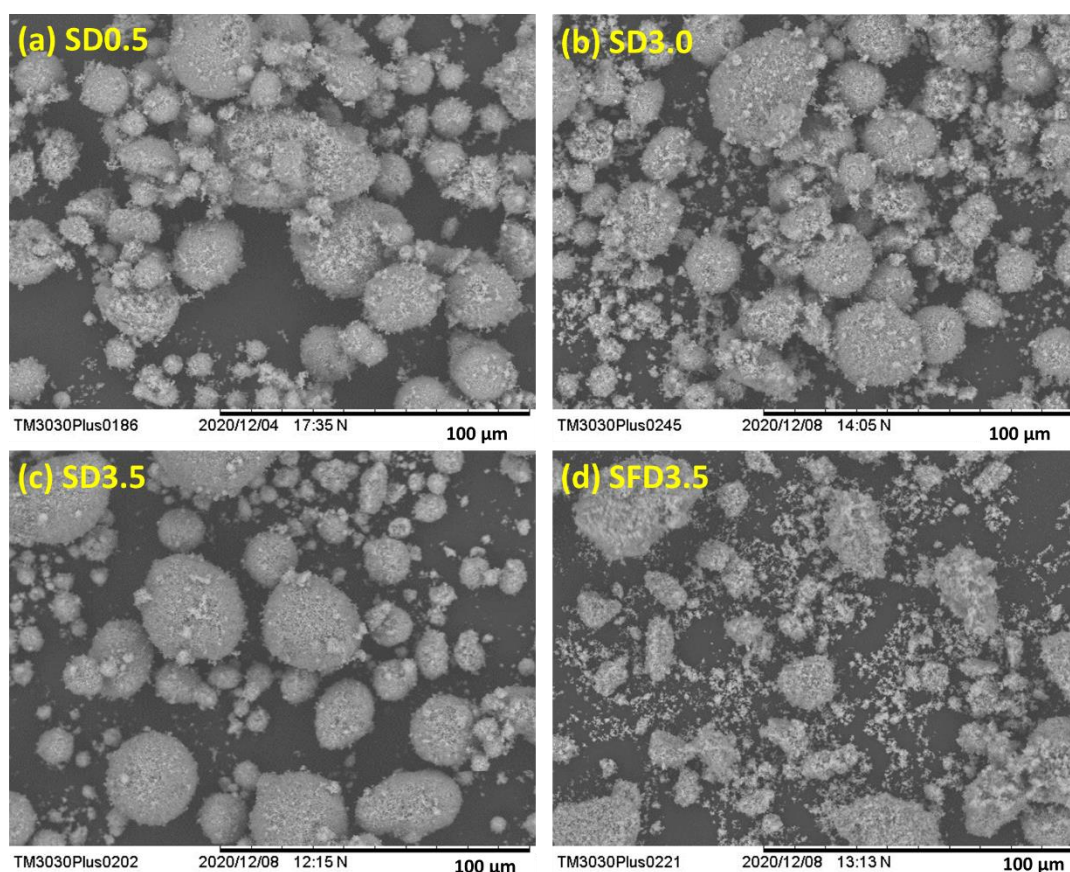


Figure 3.1 – Typical SEM images of spray dried and spin flash dried TiO_2 taken at 1000x magnification. (a) spray dried 0.5 wt% alumina, (b) spray dried 3.0 wt% alumina, (c) spray dried 0.5 wt% silica and 3.0 wt% alumina, and (d) spin flash dried 0.5 wt% zirconia and 3.0 wt% alumina. **Note:** Spray dried granules were spherical, whilst spin flash dried granules were irregular shaped.

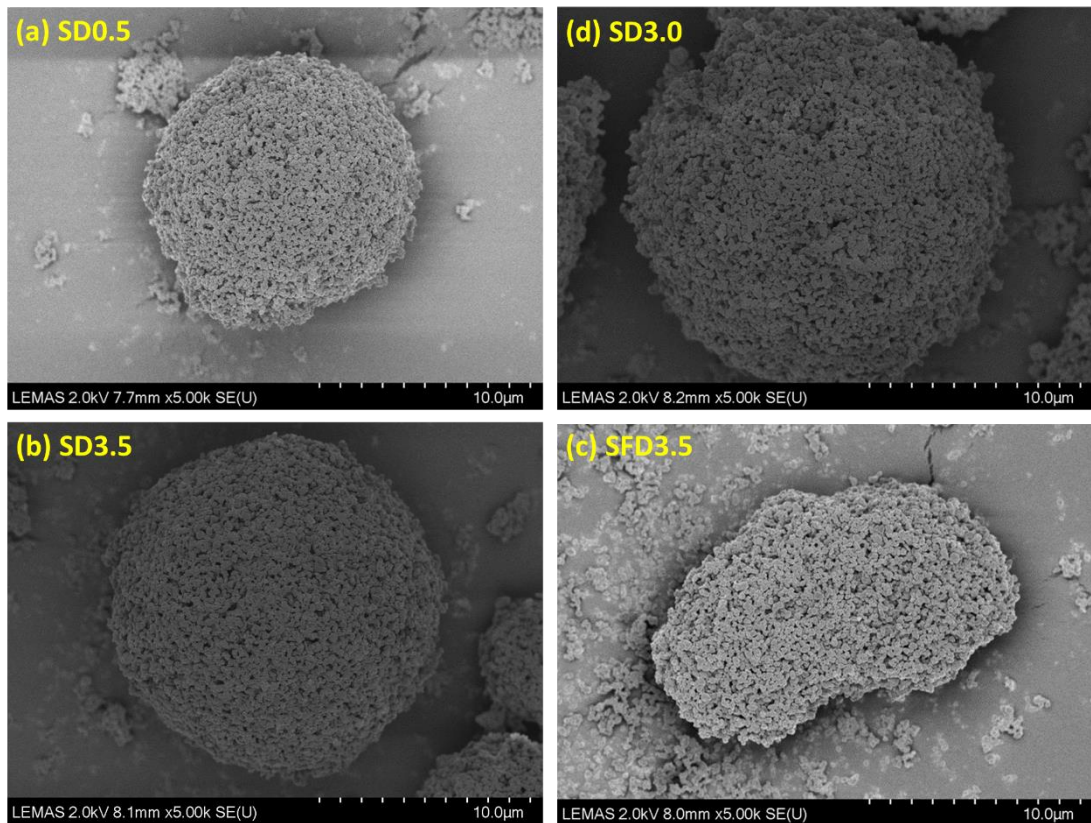


Figure 3.2 – Typical SEM images of spray dried and spin flash dried granule structures taken at 5000x magnification. Note: SEM images further highlight the spherical nature of spray dried granules and the irregular shaped spin flash dried granules.

The shape differences between spray dried and spin flash dried powders are likely to be a result of the drying methods which were utilised to prepare each powder. For spray drying, granules are formed from the drying of atomised droplets. The most stable shape a droplet can exhibit is a spherical form (Lintingre et al., 2016). Providing the suspension has been flocculated prior to spray drying and the capillary pressure of the drying droplet stays low during drying, then the atomised droplet should dry with a spherical structure (Lintingre et al., 2016). SEM micrographs for spray dried granules showed no signs of surface deformations or distorted structures which occurs during the drying of highly dispersed systems where the capillary pressure increases to such a degree it pulls the surface of the drying droplet inwards (Lintingre et al., 2016).

In contrast, the spin flash drying method of dispersing the feed material is carried out using mechanical agitation, which is used to disperse a high-viscosity paste or filter cake whilst transporting it into the drying chamber. The dispersed high viscosity feed material undergoes further mechanical dispersion when it falls vertically onto a spinning rotor. During this process, a hot gas enters and flows upwards through the chamber. As the hot air leaves the top of the

chamber, dried granules are removed from the chamber by the hot air stream, whilst the heavier wetter particles remain in the chamber for further processing (Mujumdar, 2014).

In comparison to the spray drying process, the production of particles with precise geometries in the spin flash drying process is very much uncontrolled. The granules which are formed are therefore likely to be the result of many more factors. It is probable that during the spin flash drying process, drying particulates are likely to experience many more droplet/particle collisions and impacts with the chamber walls. With further mechanical agitation by the spinning rotor at the bottom of the chamber, a particulate material with a wide range of shapes and sizes is likely to be the result. In contrast, the spray drying process is very much controlled. A lower viscosity feed material is atomized to produce droplets which do not undergo any further dispersion. If the spray drying is carried out in a co-current process, where the feed material and drying gas enter at the top of the drying chamber and the dried powder and drying gas leave the bottom of the chamber, then the process takes place in one direction. Whilst it is likely that some droplet collisions and droplet-wall collisions will still occur in spray drying, in comparison to the spin flash drying process, the number of these collisions is likely to be considerably less.

The surface of spray dried and spin flash dried granules were also imaged at a much higher 40,000x magnification. Typical images are displayed in Figure 3.3. These images clearly display assemblies of TiO_2 aggregates and crystallites. The size of the crystallites were measured using image analysis and were found to be 266, 297, 297 and 315 nm for SD0.5, SD3.0, SD3.5 and SFD3.5 respectively. The size of individual TiO_2 crystallites were as expected and were typical of TiO_2 crystallite sizes formed by the chloride process, which have optimized average sizes of 200 – 300 nm (McNulty, 2007; Auer et al., 2017; Veronovski, 2018).

The SEM images displayed in Figure 3.3 also show the coatings which have been applied to the surfaces of the TiO_2 crystallites. These coatings are more prominent in Figure 3.3b, 3.3c and 3.3d, which is consistent with the higher level of surface treatment applied. In a couple of works, it's been suggested that when the coatings are precipitated at higher levels, the surface treatments act as an adhesive, adhering TiO_2 crystallites and aggregates together (Liu et al., 2009; Zhang et al., 2009). The SEM images taken at the highest magnification for SD3.0, SD3.5 and SFD3.5 shown in Figure 3.3, do seem to support this idea.

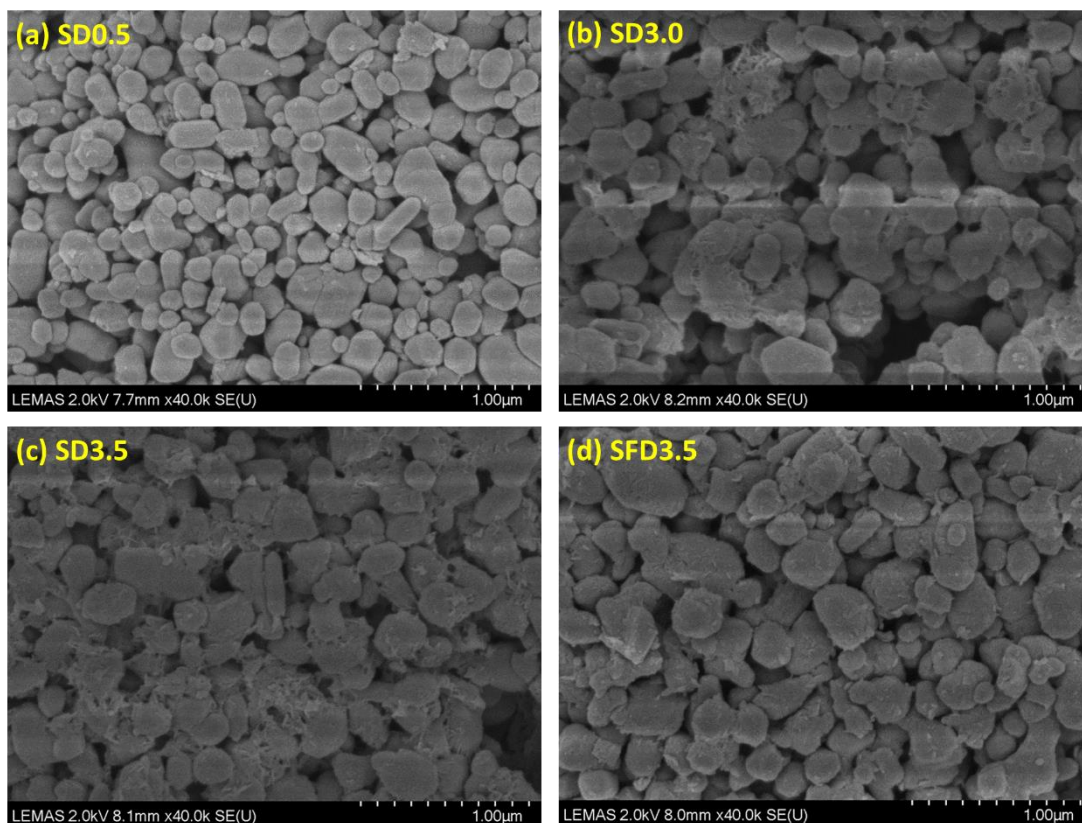


Figure 3.3 - Typical SEM images of granule surfaces taken at a magnification of 40,000x. **Note:** Surface treatments applied at higher levels can be seen in micrographs b, c and d.

3.3.2 Particle size analysis

The average particle sizes and particle size distributions of the supplied powders were determined using laser diffraction (LD) and automated static image analysis (ASIA). Before undertaking any size analysis, each powder was passed through a sieve with an aperture size of 500 μm to remove any significantly larger particles such as spray drier wall debris or large agglomerates. The influence of removing material $>500 \mu\text{m}$ on the particle size distributions can be seen in Figure A3.1 which can be found in the appendix. Unless specified, the subsequent analysis reported, for example FT4 powder rheology results were determined using material $<500 \mu\text{m}$ in size.

For material $<500 \mu\text{m}$ in size, the volume-weighted particle size distributions determined using these two particle sizing techniques are displayed in Figure 3.4 and particle sizing metrics are tabulated in Table 3.2. Overall, the distributions displayed in Figure 3.4 for both techniques compared relatively well. However, some differences between the distributions obtained for both techniques can be observed. In particular, the distributions obtained for the spin flash dried powder compared less well. Instead, the distribution obtained by LD for SFD3.5 displays material at much larger sizes and a shoulder on the distribution can also be observed. However, this shoulder is found to be absent in the Morphologi G3 distribution.

This discrepancy between these two distributions could be explained by the sampling technique which is employed by the Morphologi G3, whereby a precision made spatula is used to transfer a precise volume ($3 - 13 \text{ mm}^3$) of powder to the dispersion unit. In this work, the actual powder volume sampled was 5 mm^3 and this volume was chosen to provide effective sample dispersion and minimise particle overlap. In comparison to laser diffraction, the quantity of sample used by the Morphologi G3 to obtain the measurement is extremely small. This sampling method may also be less selective to the larger particles of spin flash dried SFD3.5, where the possibility of size segregation may occur.

One other difference noted between the distributions measured by these two particle sizing methods, is the volume of fines measured between $1 - 10 \text{ }\mu\text{m}$. This difference could be attributed to the Morphologi G3's measurement optics which has a cut-off size below $2.16 \text{ }\mu\text{m}$. Furthermore, the Morphologi G3 utilises a 5 megapixel camera and during this analysis the 5x objective lens was utilised. According to Malvern, the 5x objective lens has a particle size measurement capability between $6.5 - 420 \text{ }\mu\text{m}$ (Malvern Instruments Ltd, 2015). Therefore, the Morphologi G3 and the analysis settings chosen may actually struggle to size the smaller particles in these materials. However at $<1\%$, the actual volume of fines measured between $1 - 10 \text{ }\mu\text{m}$ by the laser diffractometer is actually miniscule and therefore it could also be argued that this difference is actually insignificant. Another possible reason to explain the presence of $1 - 10 \text{ }\mu\text{m}$ fines in the LD distributions could be due to contamination, where the unit has been tainted from a previous analysis. It is also worth mentioning here that the selected objective lens utilised by the Morphologi G3 with its particle size measurement capability of $6.5 - 420 \text{ }\mu\text{m}$ may also struggle to size the larger particles in spin flash dried SFD3.5, and therefore may be responsible/contribute to the smaller average size being measured in comparison to the values obtained by the laser diffractometer (Table 3.2).

Despite the potential disadvantages of the Morphologi G3, the distributions obtained by these two methods enables two different measurement principles to be compared. The dispersion and working principles of laser diffraction are more dynamic in nature, whilst once dispersed onto the glass slide, the analysis principles of the Morphologi G3 is more static in nature. Therefore, by comparing the results obtained by laser diffraction, the Morphologi G3 can allow unknowns such as breakage and auto-agglomeration to be discounted from the analysis. This is because the particle images obtained during Morphologi G3 analysis can be examined for breakage and auto-agglomerates. Furthermore, the data can be treated with subsequent post data processing. Since, the distributions obtained using both techniques compare relatively well, the obtained data suggests that little breakage or auto-agglomeration has occurred during the laser diffraction analysis. However, due to the draw backs of the Morphologi G3 technique, in this work, laser diffraction was thought to be the most effective method for characterising the size distributions

for spray dried and spin flash dried titanium dioxide. Therefore in this work, the particle sizing results obtained from laser diffraction were used as a benchmark and are therefore referred to in proceeding chapters.

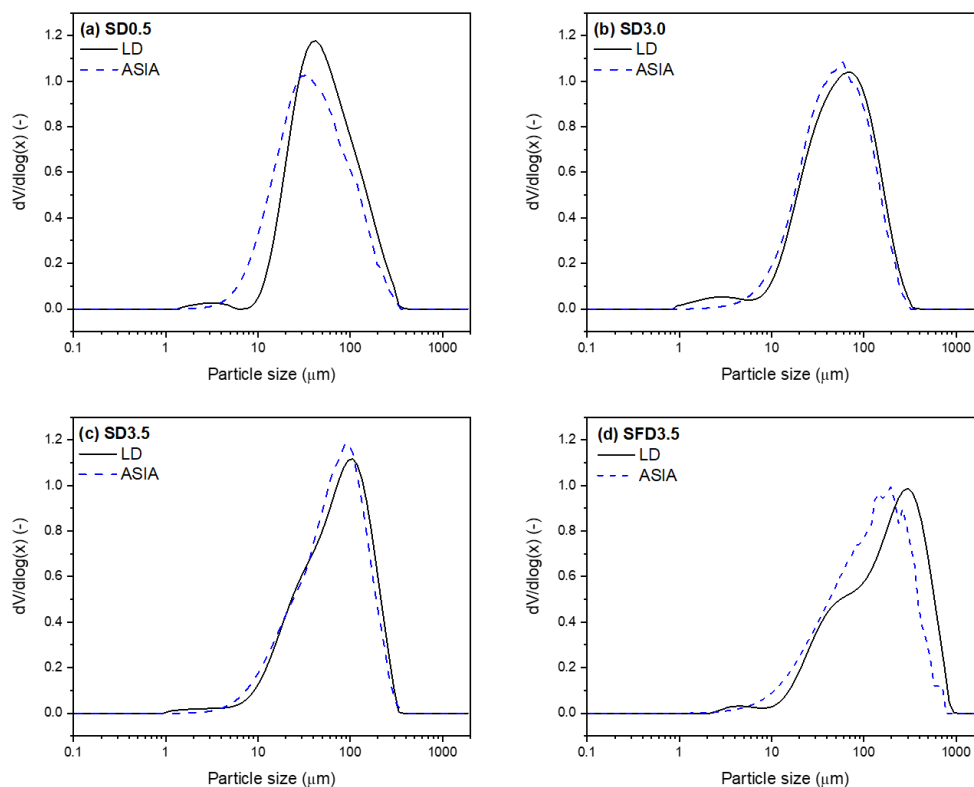


Figure 3.4 – A comparison of the particle size distributions obtained using laser diffraction (LD) and automated static image analysis (ASIA) for spray dried and spin flash dried titanium dioxide. **Note:** AISA was undertaken using the Malvern Morphologi G3 instrument.

Table 3.2 – Particle size metrics determined by laser diffraction and automated static image analysis for spray dried and spin flash dried titanium dioxide.

Method	Powder	$D[v,5]$ (μm)	$D[v,10]$ (μm)	$D[v,50]$ (μm)	$D[v,90]$ (μm)	Span	$D[4,3]$ (μm)	$D[3,2]$ (μm)
Laser diffraction	SD0.5	15	20	49	143	2.5	67	35
	SD3.0	10	17	54	144	2.4	69	26
	SD3.5	12	19	72	176	2.2	86	36
	SFD3.5	21	32	172	475	2.6	216	70
Automated static image analysis	SD0.5	-	14	37	111	2.6	58	31
	SD3.0	-	17	49	125	2.2	67	38
	SD3.5	-	18	69	146	1.9	84	44
	SFD3.5	-	27	124	312	2.3	165	66

To aid comparison between samples, Figure 3.5 displays the normalised volume and cumulative volume distributions, which were determined by laser diffraction on single plots. Also listed in Table 3.2 is a full list of particle sizing metrics which were also determined by laser diffraction and the Morphologi G3. For all materials, the particle size distributions were found to exhibit log normal distributions, however on a logarithmic scale the distributions displayed various levels of skewness. The distribution obtained for SD0.5 displayed a negative skewness, whilst the distribution obtained for SD3.0 displayed a bell shaped curve with symmetry, i.e. skewness of 0. In contrast, the distributions obtained for SD3.5 and SFD3.5 exhibited some positive skewness. A negative skewness indicates the distribution is skewed to the smaller particles of the distribution, whilst a positive skewness shows that the distribution is skewed to the larger particles in the distribution.

Considering the percentiles, the $D[v,10]$, $D[v,50]$ and $D[v,90]$ obtained for SD0.5 and SD3.0 were found to very similar, which shows that these two spray dried materials have distributions containing similar sized particles/granules. However, a size difference does exist, with SD3.0 showing larger granules with a $D[v,50]$ of 54 μm , whereas SD0.5 has a $D[v,50]$ of 49 μm . The $D[v,50]$ obtained for spray dried SD3.5 was determined to be 72 μm and is therefore significantly larger than the $D[v,50]$ obtained for spray dried SD0.5 and SD3.0. Larger still is the $D[v,50]$ obtained for spin flash dried SFD3.5, which was determined to have a value of 172 μm . As discussed earlier, the average particle size is an important factor to consider here because the interparticle forces become significantly stronger than the gravitational forces for particles less than $\sim 100 \mu\text{m}$. When the interparticle forces are stronger than the gravitational forces, the powder structure can sustain loose assemblies of particles and the powder is said to be cohesive. In contrast, when the gravitational forces dominate, the powder is said to be non-cohesive (Hassanpour et al., 2019). Therefore, based upon the average particle sizes, these results would suggest that SD0.5 is the most cohesive powder whilst SFD3.5 is the least cohesive powder. Based upon size, the order of cohesivity for these four powder could predicted to be $\text{SD0.5} > \text{SD3.0} > \text{SD3.5} > \text{SFD3.5}$.

One other difference which can be found in the LD particle size analysis for SD0.5 and SD3.0 is within the $D[3,2]$ value, which is 35 and 26 μm respectively (Table 3.2). For SD3.0, its $D[3,2]$ value is therefore smaller in comparison to SD0.5. This difference can be attributed to a greater number of particle fines present within the distribution of SD3.0, which increases its surface area. The presence of fine particles adhered to granule surfaces were also noted during microscopic analysis and furthermore, a comparison of the $D[v,5]$ and $D[v,10]$ results shows that the particle fines in SD3.0 are actually smaller than those present in SD0.5, which means there is a greater number of fine particles present in SD3.0. The presence of particle fines is particularly highlighted here as the fine particle fraction can influence bulk powder handling behaviour. For example,

Madian et al. (2020) studied the influence of the particle fine fraction on the rheological properties of uranium dioxide powders and showed that as the particle fines content increased from 10 – 100%, the powder flowability became poorer. Of further note, the particle fines content for SD3.5 is also similar to SD3.0, whilst the size of the fines content of SFD3.5 is the largest of the four powders.

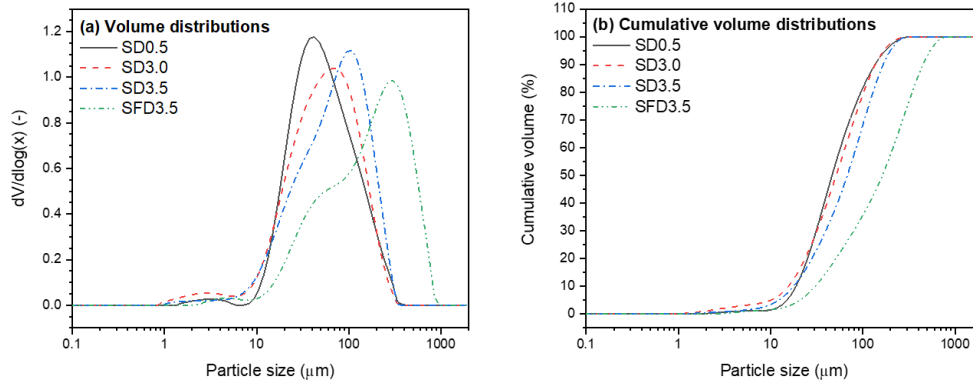


Figure 3.5 – Normalised volume (a) and cumulative volume (b) distributions determined by laser diffraction for spray dried and spin flash dried titanium dioxide. Note: these distributions are plotted on the same plots to aid comparison.

3.3.3 Particle shape analysis

The morphologies/shapes of granules were further assessed using ASIA, where the High Sensitivity Circularity (*HSC*) shape factor was used to assess granule shape. The *HSC* is defined as the ratio of the particles projected area, *A* to the square of its perimeter, *P* multiplied by 4π , Equation 3.2;

$$HSC = \frac{4\pi A}{P^2} \quad (3.2)$$

The *HSC* is an indicator of the closeness of a particle to a perfect circle. *HSC* values range from 0, highly irregular to 1, perfect circle (Ulusoy and Kursun, 2011).

Displayed in Figure 3.6 is the *HSC* data as a function of the Circle Equivalent (CE) Diameter for all four powders. In each plot, each data point represents a single particle/granule. Overall, the distributions show that the majority of the spray dried and spin flash dried granules have an *HSC* of 0.75 – 1.00. The plot displayed for SFD3.5 also shows there is a greater number of particles located at larger sizes $>75 \mu\text{m}$. Whereas, for SD0.5 there is a greater number of particles located at smaller sizes $<75 \mu\text{m}$. The plot for SD3.0 also shows a similar distribution of particles as that for SD0.5. The size results are therefore consistent with those determined by laser diffraction.

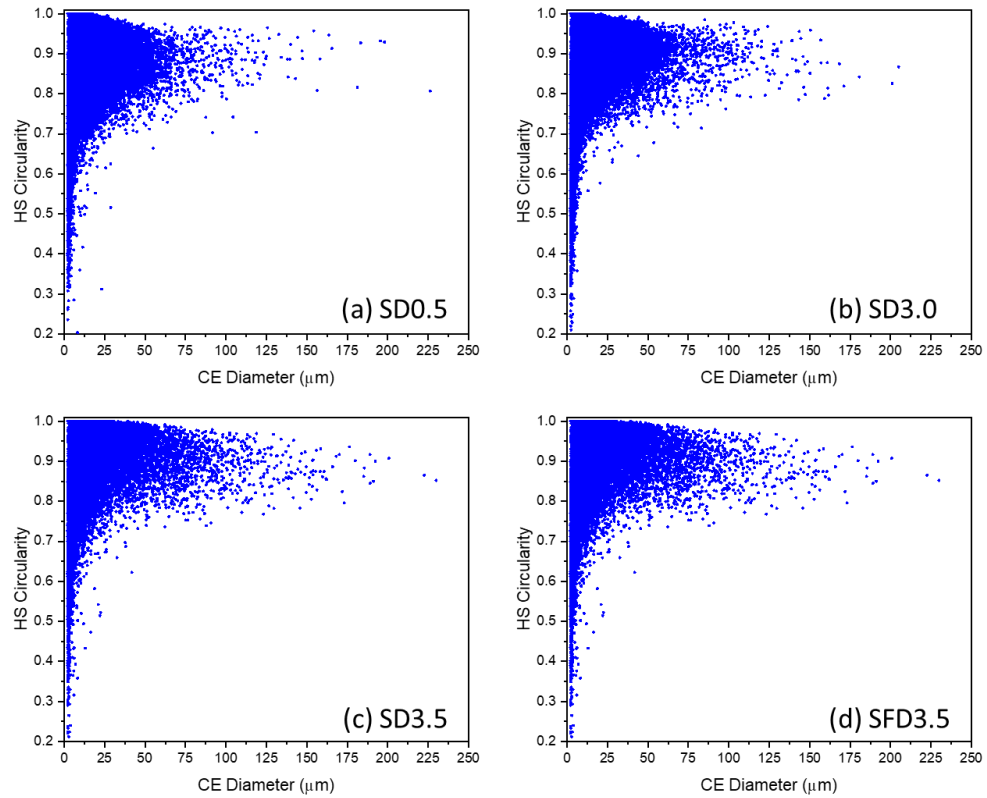


Figure 3.6 - *HSC Circularity data as a function of CE Diameter for spray dried and spin flash dried titanium dioxide.*

To aid further comparisons, also reported in Figure 3.7, are *HSC* shape factors for specific particle sizes and for specific areas of each distribution. For each stated particle size, the mean *HSC* reported is based upon $\pm 10\%$ of the stated particle size. For the reported $D[v,10]$, $D[v,50]$ and $D[v,90]$, the mean *HSC* value is based upon 5% of the distribution located at the stated percentile. Overall, regardless of whether the *HSC* shape factors are compared at specific particle sizes or specific areas of the distribution, the data highlights the greater sphericity of the spray dried granules in comparison to the spin flash dried powder. This shape analysis is also consistent with the shapes of granules observed during microscopic observations. Recall earlier in microscopic observations where spin flash dried granules were noted to be less spherical in comparison to the spray dried granules.

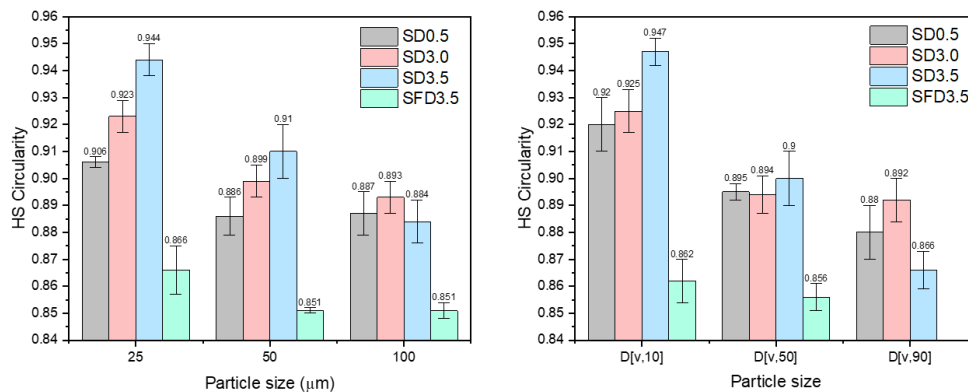


Figure 3.7 - Shape analysis using the High Sensitive Circularity Shape factor, where the HSC is reported at specific particle sizes and at specific areas of each distribution.

3.3.4 Moisture sorption and specific surface area

The moisture sorption of the supplied materials were investigated using dynamic vapour sorption (DVS). With water as a probe molecule, DVS experiments allow the moisture content of a powder as a function of changes to the relative humidity (RH) to be understood. The moisture sorption isotherms obtained from this analysis are displayed in Figure 3.8.

In terms of total moisture adsorbed, the isotherms showed that SD0.5 adsorbed a total moisture content of 0.75 wt% at 90% RH, whilst SD3.0, SD3.5 and SFD3.5 adsorbed total moisture contents of ~2 wt% at 90% RH. These results were found to be consistent with those of Li (2019) who also obtained a total moisture content of ~2 wt% at 90% RH with 3 wt% alumina coated TiO₂. Day (1990) also states that water sorption is higher for durable pigments which feature higher levels of coatings. This significant difference in moisture sorption for SD3.0, SD3.5 and SFD3.5 in comparison to SD0.5 can therefore be accounted for by the higher levels of surface treatments applied to these materials.

The isotherms also showed that the moisture content of each powder varied very little (≤ 0.3 wt%) between a relative humidity of 20 – 40%, which is a typical region where the humidity of a laboratory may fluctuate between. Therefore, slight changes to the laboratory relative humidity during powder characterisation, especially for bulk powder flow properties was not thought to be significant enough to effect the measurements made in subsequent chapters.

DVS isotherms can also reveal other information such as surface structure and this information can be obtained from the shapes of the sorption curves. For the four powders studied, the moisture sorption isotherms displayed similar shaped curves, where the isotherm begins with a steep incline between 0 - 20% RH, this region is followed by a shallower incline between 20 - 70% RH, which

afterwards is followed by another steeper incline. According to IUPAC (International Union of Pure and Applied Chemistry), the majority of adsorption isotherms can be grouped into the six main types (Sing et al., 1982). According to this classification system, the sorption isotherms shown in Figure 3.8 were found to exhibit the Type II isotherm, which is also consistent with the work of Li (2019). The Type II isotherm is a typical isotherm obtained during the analysis of non-porous or microporous (pore sizes <2 nm) absorbents (Sing et al., 1985) and represents unrestricted mono-layer and-multilayer adsorption. The transition between the first steep incline and the shallower region is thought to be the stage where monolayer coverage is complete and where multi-layer adsorption begins (Sing et al., 1982).

The isotherms obtained for SD3.0, SD3.5 and SFD3.5 were also found to exhibit hysteresis loops, whilst for SD0.5 a hysteresis loop was found to be absent. The absence of a hysteresis loop in SD0.5 can be seen much more clearly in Figure A3.3a (See appendix), where the y-axis for SD0.5 has been rescaled. According to Sing et al. (1985), hysteresis loops are associated with capillary condensation in mesopore (2-50 nm pore sizes) structures and as stated by IUPAC, it is possible to classify hysteresis loops into four main categories (Sing et al., 1982; Sing et al., 1985; Sing and Williams, 2004). According to this classification system, the hysteresis displayed for SD3.0, SD3.5 and SFD3.5 is of the Type H3 hysteresis loop. The Type H3 has been observed with aggregates of plate-like particles which give rise to slit-shaped pores (Sing et al., 1982; Sing et al., 1985) or pore networks which consist of macropores (pore sizes >50 nm) which are not completely filled with pore condensate (Thommes et al., 2015). The presence of Type H3 hysteresis loops therefore provides an indication towards the porous structural nature of the alumina films applied to the surface of TiO_2 .

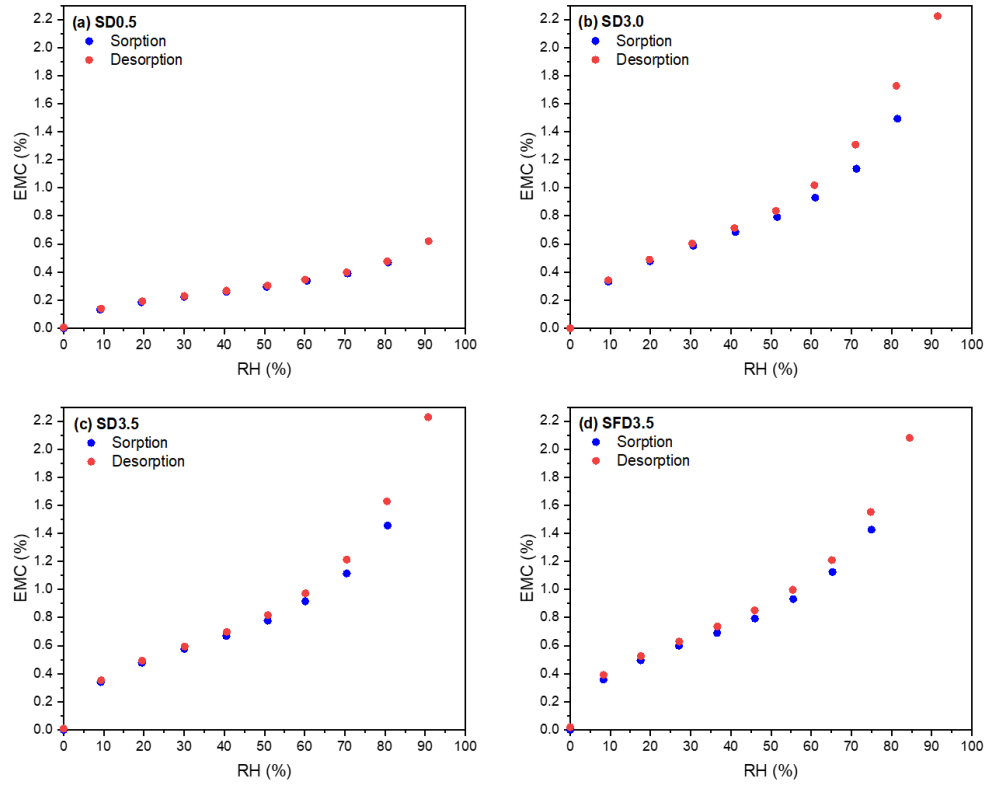


Figure 3.8 - Dynamic vapour sorption (DVS) isotherms for spray dried and spin flash dried titanium dioxide. EMC – Equilibrium Moisture Content, RH – Relative Humidity.

To determine the specific surface area's (SSA) of the supplied powders, further vapour sorption analysis was undertaken using nitrogen. The nitrogen adsorption isotherms from this analysis can be found displayed in Figure A3.2. These isotherms were analysed against the linear form of the Brunauer Emmett Teller (BET) model, Equation 3.3 (Brunauer et al., 1938). During this analysis, the BET model was applied to the regions of $0.05 < P/P_0 < 0.35$ to determine the specific surface area's (SSA) of the supplied powders.

$$\frac{P}{v(P_0 - P)} = \frac{P/P_0}{v(1 - P/P_0)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} \left(\frac{P}{P_0} \right) \quad (3.3)$$

In Equation 3.3, P is the vapour pressure, whilst P_0 is the atmospheric pressure (101,325 Pa), v_m is the monolayer adsorbed nitrogen volume per gram of sample, whilst v is the absorbed nitrogen volume per gram of sample and c is the BET constant. v_m is related to the specific surface area (SSA) via Equation 3.4 (Hintz et al., 2014);

$$SSA = \frac{P}{RT} [v_m A_m N_a] = \frac{1}{V} [v_m A_m N_a] = \frac{1}{0.02214} [v_m A_m N_a] \quad (3.4)$$

where A_m is the molecular cross sectional area of a nitrogen molecule, which has a value of 0.162 nm² (Hintz et al., 2014), N_a is Avagadro's constant and V is the molar volume of nitrogen at standard temperature and pressure conditions, which has a value of 0.02214 m³/mol.

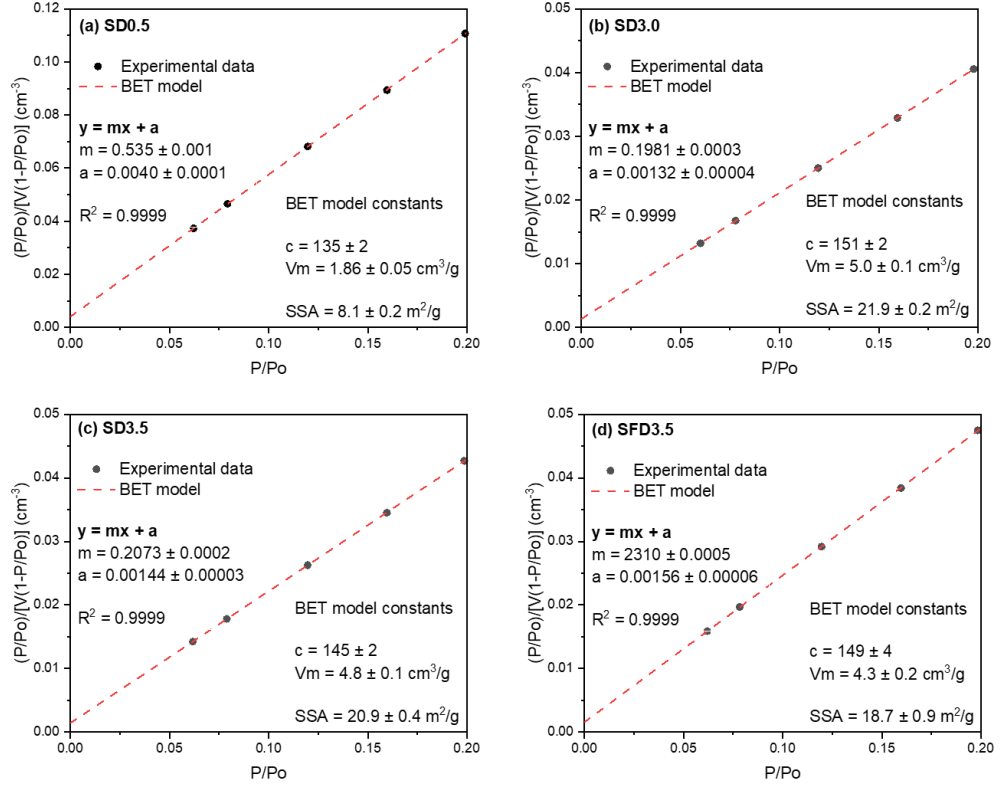


Figure 3.9 - BET specific surface area (SSA) plots obtained by nitrogen adsorption for spray dried and spin flash dried titanium dioxide.

The parameters obtained from the BET model and the determined SSA's can be found reported in Figure 3.9 and in Table 3.3. The obtained specific surface area (SSA) values showed that SD0.5 which contains only 0.5 wt% alumina coating exhibits a surface area of 8.1 m²/g. In contrast, the surface areas of SD3.0, SD3.5 and SFD3.5 are larger with surface areas of 21.9, 20.9 and 18.7 m²/g. It is well known that the surface area of titanium dioxide increases significantly with the addition of alumina coatings (Day, 1974; Day and Egerton, 1987; Siwińska-Stefańska et al., 2008; Auer et al., 2017; Li, 2019). Therefore, in this work, our results are consistent with those reported by others. Interestingly, for a low alumina surface treatment of 0.5 wt%, the surface area does not increase significantly. In fact, the surface area for a 0.5 wt% alumina surface treated TiO₂ is similar to the surface area of TiO₂ without additional alumina coating (Li, 2019).

The larger surface area of SD3.0, SD3.5 and SFD3.5 is also likely to be responsible for the adsorption of greater moisture contents. At any one particular area/location on a particle, the

surface moisture content is likely to be similar for all four powders. This is shown in Table 3.3 where a ratio of water mass (in units of wt%) to SSA (in units of m²/g) is calculated. The calculated ratio's for all four powders range between 0.030 – 0.036 and are very similar. Therefore, for powders which feature higher levels of surface treatments, the larger surface area provides a greater number of sites for water molecules to adsorb/desorb. This could also mean that the presence of any moisture is likely to have a similar influence on bulk powder handling characteristics such as cohesion and powder flowability.

Table 3.3 - Parameters estimated from the BET model using nitrogen as a probe molecule.

Parameter	SD0.5	SD3.0	SD3.5	SFD3.5
<i>c</i>	135 ± 2	151 ± 2	145 ± 2	149 ± 4
<i>v_m</i> (cm ³ /g)	1.86 ± 0.05	5.0 ± 0.1	4.8 ± 0.1	4.3 ± 0.2
<i>R</i> ²	0.9999	0.9999	0.9999	0.9999
SSA (m ² /g)	8.1 ± 0.2	21.9 ± 0.2	20.9 ± 0.4	18.7 ± 0.9
m _{H2O} /SSA*	0.033	0.030	0.032	0.036

*Ratio of water mass (determined at 40% relative humidity) to SSA. Units: wt%/(m²/g).

3.4 Conclusions

Supplied spray dried and spin flash dried titanium dioxide powders were characterised using SEM, laser diffraction, ASIA, DVS and nitrogen sorption. Microscopic observations and shape analysis revealed that spray dried granules were spherical, whilst spin flash dried granules exhibited irregular non-spherical shaped granules. These shape differences were attributed to their respective drying methods. Later, size analysis via laser diffraction showed that the spray dried powders SD0.5 and SD3.0 featured similar distributions of similar size particles with a *D*[v,50] of approximately 50 µm, however the size analysis also indicated that a slight size difference existed with SD3.0 displaying slightly larger sized granules in comparison to SD0.5. Spray dried SD3.5 exhibited a slightly larger *D*[v,50] of 72 µm, whilst spin flash dried SFD3.5 displayed the largest granule sizes at 172 µm. Based upon size, the relative cohesivity of these four powders is could be predicted to be SD0.5<SD3.0<SD3.5<SFD3.5. However, the non-spherical shape of SFD3.5 is also likely to impact this order and the bulk handling characteristics of SFD3.5 such as its powder flowability. Vapour sorption analysis revealed that powders with higher levels of coatings absorbed greater quantities of moisture due to their larger surface areas. However, the actual moisture sorption per surface area is similar for all four powders and therefore, the influence of moisture is likely to have a similar influence on interparticle cohesion and powder

flowability. In proceeding chapters, these findings prove significant for understanding the bulk handling behaviour of spray dried and spin flash dried titanium dioxide.

Chapter 4 – Powder flowability

4.1 Introduction

In bulk solids processing, good powder flow characteristics are vital in order for a given powder to be transported or conveyed between unit operations. If a powder does not flow well, then its bulk handling behaviour will be significantly affected resulting in process problems such as blockages which can ultimately lead to a manufacturing process stalling to a standstill. Therefore, an understanding of powder flowability is vital for understanding how a given powder will perform during processing.

The flowability of a powder can be dependent on many factors. Particle properties such as size and shape will be significant, including other powder characteristics such as bulk density. Moreover, the process used to handle the powder will define the stress conditions in which the powder is subjected to and ultimately the behaviour that the powder displays. Due to their ability to rearrange under stress, powders can display a complex behaviour and can exhibit qualities similar to a solid, liquid or a gas depending on the way the particles interact (Hassanpour et al., 2019).

In understanding powder flow, it can be useful to consider the four rheological states in which powder flow can be classified. These rheological states help to provide a simplistic overview to the different types of powder flow that are possible. Also known as flow regimes of which there are four, these rheological states are termed static, Quasi-static, intermediate and rapid granular (Tardos et al., 2003; Francia et al., 2021). When a powder displays the static flow regime, it exhibits a static state and displays no motion. A yield condition is used to define the point at which the powder starts to deform. In the Quasi-static flow regime, particle movement is very slow, the interparticle interactions occur by frictional sliding and the powder exhibits a dense state. Within the intermediate flow regime, particle interactions occur via collisional and frictional interactions. When particles move so fast where only short range collisions occur, the powder is said to display the rapid granular flow regime. These flow regimes can be identified by the magnitude of their dimensionless shear rates, which are 0, >0 to ~ 2 , ~ 2 to 3 and >3 for the static, Quasi-static, intermediate and rapid granular flow regimes respectively (Tardos et al., 2003; Hassanpour et al., 2019). The presence of a stress-strain relationship can also be used to differentiate between the Quasi-static and dynamic flow regimes (intermediate and rapid granular).

Many techniques are available to characterise the flow properties of powders and a number of studies have investigated the flow behaviour of powders using different methods, see for example Lecturia et al (2014) and Krantz et al (2009). Lecturia et al. (2014) concluded that powder flow properties cannot be predicted by a single indicator and several characterization methods which

apply a range of conditions are required to ensure a complete understanding. In doing so, this approach can provide better insight into the powder-process relationship. Krantz et al. (2009) also came to a similar conclusion stating that characterization techniques which were more dynamic were better for predicting fluidisation, whilst techniques which were more static were more suitable for predicting agglomeration. Krantz et al. (2009) also found that results from static and dynamic characterizations do not necessarily agree and can depend upon the applied stress states. The findings from these authors are likely due to the fact that different techniques subject powders to different sets of conditions and consequently, the results from these tests are also interpreted under these circumstances. Different powder flow techniques were also designed for different purposes and to measure specific flow properties of a powder, which means they may have limited application outside of their designed use. Furthermore, depending on the conditions applied to the powder, different types of particle interactions will occur and these interactions will govern the rheological state of the powder. For example, the Quasi-static flow regime is dominated by frictional interactions only, whereas the rapid granular regime is governed by collisional interactions.

Before thinking about characterising powder flow, it can also be useful to consider the process and the behaviours that a powder will display during handling. In doing so, techniques can be carefully selected to mimic these behaviours and understand how the powder may behave during processing. In terms of spray drying, as soon as the particles are formed they will exit the spray drier where the powder will then be separated from the drying gas. During this process, the powder is likely to experience many of the rheological states described previously, especially if the solid fraction increases and the powder begins to build-up. Therefore, the powders under study will experience a range of shear rates, exhibit various solid fractions and the powder particles will be subjected to frictional and collisional interactions. Thus, it was felt necessary to subject the supplied powders to a range of conditions in order to fully characterise and understand their flow properties.

Therefore in light of this information, a number of techniques were employed to subject the supplied powders to a range of conditions and investigate their flow behaviour. Moreover, characterisation techniques utilising dynamic as well as Quasi-static methodologies were thought to be useful to understand the powder when it is in motion, as well as its strength when it is present in a consolidated form. In doing so, this approach of applying several techniques has enabled a relationship between the process scale and the lab scale testing to be developed. In fact, this approach also seems to be the best method which is available to the powder technologist. The techniques which have been utilised in this work were bulk and tapped density testing, compressibility tests, static Angle of Repose (AoR) measurements, Schulze shear cell testing and FT4 powder rheology. In particle science and powder technology, these techniques have become

well established for studying the flow behaviour of particulate solids and in the discussions which follow, justifications are provided for their use in this study.

The bulk density of a powder is related to particle mobility and the ability of particles to pack, which are in turn related to the flowability of the powder at the bulk level (Hassanpour et al., 2019). According to Abdullah and Geldart (1999), relative changes in bulk density can be very sensitive indicators to changes in the structural strength of a loosely compacted powder and hence of its flow characteristics. Therefore, in this work, bulk and tapped density measurements were employed to study powder density and packing between two different states. During these tests, the powder density was first determined by pouring a known mass of powder into a cylinder. Later, the powder was subjected to tapping, where the powder particles were rearranged into a more compact structure, and their relative resistance to rearrangement was used to reveal their unique characteristics, whilst indirectly assessing their flow behaviour.

Similarly to bulk and tapped density measurements, compressibility measurements were also utilised to reveal further powder characteristics. Whilst compressibility is not a direct measure of flowability, this metric provides a useful indicator as to whether a powder is likely to be cohesive or free flowing (Fu et al., 2012). Apparently, cohesive powders which display poor flow behaviour have large voids of entrained air and as a result are highly compressible (Shur et al., 2008; Lecturia et al., 2014; Ludwig and Miller, 2015). In contrast, free flowing powders pack more efficiently and have little entrained air which therefore results in low compressibility. Therefore, the more compressible a powder is, the less free-flowing it will be; the less compressible, the more flowable (Carr, 1965). Furthermore, compressibility measurements were also used to study packing, but instead of subjecting the powder to tapping as for tapped density measurements, supplied powders experienced a different set of conditions, where powders beds were subjected to deformation and rearrangement via an applied normal force. Consequently, the change in powder volume was used to indirectly assess powder flowability.

The AoR is another well-established technique for investigating powder flow and can be used to rank powders for their flowability (Hassanpour et al., 2019). According to Geldart et al. (2006), the AoR has often met industrial and academic needs for a simple and quick test that can disclose changes in the flow properties of powders as they pass through processing and handling equipment. The AoR has also been used by Lumay et al. (2012) to characterise powder flow in the static flow regime. Therefore in this work, the static AoR was deemed useful for investigating powder flowability for the supplied materials, where powder semi-cones were formed against a Perspex wall via a vibrating chute and hopper. The radius and height of which was then used as method to evaluate powder flow.

The application of shear cell techniques for evaluating powder flow properties for the design of hoppers and silos was first pioneered by Jenike (Fitzpatrick et al., 2004). Apparently, powder storage and handling in silos and hoppers are examples of operations where bulk powder handling is characterised by slow movements of the system or static conditions, but furthermore this type of flow behaviour is also known to be common in other process units (Hassanpour et al., 2019). Moreover, shear cell testers are also known to be valuable tools for understanding the influence of particle properties on the macroscopic bulk response (Shi et al., 2018). According to Ghadiri et al. (2020) and Francia et al. (2021), shear cell testing can also be used to characterise powder flowability in the Quasi-static flow regime. Therefore due to these qualities, shear cell tests were employed in this work to investigate powder flow. By subjecting the powder to consolidation and then shearing, the shear test results have provided insights with regards to the relative strengths of the consolidated powders and the agglomerated structures which can be formed during conveying.

Powder rheometers such as the FT4 powder rheometer (Freeman Technology Ltd) were primarily developed to measure powder flowability under dynamic conditions (Freeman et al., 2017). This technique essentially subjects a powder bed to agitation via a rotating blade whilst measuring the work done. Under confined and unconfined conditions, at various flow rates and aerated states, a number of metrics can be obtained using this method. Furthermore, Hare and Ghadiri (2017) have also analysed the stress and strain rate of the FT4 powder rheometer and their results have suggested that the FT4 powder rheometer may be capable of operating in the dynamic flow regimes. Therefore in this work, the FT4 powder rheometer was employed to study dynamic powder flow and understand how the supplied powders behave when in motion.

4.2 Materials and methods

4.2.1 Solid density

Solid (true/particle/matrix) density measurements were undertaken using a helium pycnometer (Pycnomatic ATC, ThermoFischer Scientific, Massachusetts, USA). A solid powder mass of approximately 2.4 ± 0.5 g was used during the analysis.

4.2.2 Bulk and tapped density

Bulk and tapped density measurements were undertaken using a tap volumeter (Copley Scientific, UK). A 250 cm^3 measuring cylinder was filled with approximately 170 - 200 g of powder and the bulk density was determined from the sample mass and its bulk volume. To determine the tapped density, the measuring cylinder underwent 1250 taps and the tapped volume was recorded. This was then followed with a further 1250 taps. If the tapped volume changed by more than 2 cm^3 ,

the sample underwent a further 1250 taps. The bulk and tapped densities were then determined from the sample mass and the initial and final tapped powder volumes.

4.2.3 FT4 compressibility

Compressibility tests were undertaken using the FT4 powder rheometer and the standard compressibility program. A 24 mm × 10 ml split sample vessel was employed. At the beginning of the test, the powder was conditioned using a 23.5 mm blade and then split to obtain a precise volume of conditioned powder with a reproducible packing state. Afterwards, the blade is changed to a vented piston and compressed at pressures of 1 – 15 kPa. The powder compressibility was then computed based on the percentage change in powder volume.

4.2.4 Static angle of repose

In this work, the method reported by Geldart et al. (2009) was used to determine the poured static angle of repose (AoR). During tests, a Mark 4 AoR tester (Powder Research Ltd) was used. By using the vibrating chute and hopper, 30 g of powder sample was used to form semi-cones of powder against a vertical Perspex wall.

4.2.5 Schulze shear cell testing

In order to evaluate powder flow properties in the quasi-static flow regime and medium to high consolidation conditions, a Schulze Ring Shear Tester (RST-XS, Dietmar Schulze, Wolfenbüttel, Germany) was employed. Powder samples were loaded into a medium sized sample cell and underwent a pre-consolidation stress. Following, pre-consolidation, the sample was sheared until steady state flow was achieved. Upon an applied normal stress, the sample was then sheared to the point of incipient failure, whilst measuring the torque, which is then subsequently converted to a shear stress. During testing, this would provide an individual point (τ, σ) on a yield locus diagram. By repeating the procedure of shearing the specimen to the point of steady state flow and using gradually increasing normal stresses, a series of points on a yield locus diagram were constructed. During testing, shear normal stresses of 25, 38, 51 and 65% of the pre-consolidation stress, σ_p were employed. For all samples, a family of yield loci were determined at pre-consolidation stresses of 1.0, 3.0, 5.0 and 7.0 kPa

4.2.6 FT4 stability and variable flow rate

In order to access the powder flow properties under dynamic conditions, an FT4 Powder Rheometer (Freeman Technology, UK) and its stability and variable flow rate program was used. The FT4 powder rheometer was fitted with a rotating blade with a diameter of 23.5 mm and a helix angle of 5°. Powder samples were also loaded into a 25 mm x 25 ml split sample vessel.

4.3.1 FT4 aeration

The sensitivity of powder flow properties to aeration was investigated using an FT4 Powder Rheometer (Freeman Technology, UK) equipped with an aeration control unit (ACU) and by using the standard aeration program. The FT4 powder rheometer was fitted with a rotating blade with a diameter of 23.5 mm (helix angle of 5°) and powder samples were loaded into a 25 mm x 35 ml sample vessel fitted with a porous aeration base through which air was introduced. The aeration method consisted of 7 test cycles and for each test cycle the flow energy was measured at a specific air velocity. The air velocities which were utilised ranged from 0 – 10 mm/s and increased at increments of 2 mm/s.

4.3 Results and discussion

4.3.1 Solid, bulk and tapped densities

The results from solid, bulk and tapped density measurements can be found listed in Table 4.1. With regards to the solid density measurements, these values were all found to range between 3.99–4.07 g/cm³. The density of rutile TiO₂ is approximately 4.23 g/cm³ and the surface treatments alumina, silica and zirconia have solid densities of 3.95, 2.65 and 5.68 g/cm³ respectively. For spray dried TiO₂ and spray dried 3 wt% alumina coated TiO₂, Li (2019) obtained solid densities of 4.22 and 4.13 g/cm³ respectively. Therefore, the results obtained in this work seem more than reasonable.

In terms of bulk densities, the spray dried granules were found to have values ranging from 791 – 927 kg/m³. In contrast, spin flash dried SFD3.5 was found to have a much larger bulk density of 1050 kg/m³. A similar trend is also observed for the tapped densities. Since the solid densities of all four powders were determined to have similar values, these results suggest that the packing ability of SFD3.5 is much better than the spray dried powders. According to Abdullah and Geldart (1999), a powder with a strong structural strength will have a low bulk density as it will resist collapse when dispersed in a container, whilst a powder with a weaker strength will collapse more easily and will therefore have a higher bulk density. Therefore, the lower bulk densities obtained for the spray dried powders can be accounted for by their higher structural strength. When present in a confined space, the stronger structural strength of the spray dried powders prevents them from collapsing. In contrast, SFD3.5 has a lower structural strength which therefore must allow it to pack much better. When compared on the basis of bulk and tapped density, the packing ability of the spray dried materials is therefore likely to suffer due to their greater cohesive nature. The source of this cohesiveness is more than likely due to the relative granule sizes in each powder rather than factors such as surface roughness or surface composition. This is because size is cubed

for the gravitational forces, whilst size has the power of unity for the interparticle forces such as van der Waals. An increase in size also significantly reduces surface area decreasing the numbers of interparticle forces which can form. Therefore, the bulk and tapped densities appear to correlate with size.

In light of the work of Li (2019) who prepared spray dried TiO_2 and spray dried 3 wt% alumina surface treated TiO_2 , the bulk and tapped densities reported in this work were found to be similar. Li (2019) obtained a bulk density of $862 \pm 3 \text{ kg/m}^3$ and a tapped density of 965 kg/m^3 for spray dried TiO_2 , whilst for spray dried 3 wt% alumina surface treated TiO_2 , a bulk density of $1025 \pm 7 \text{ kg/m}^3$ and a tapped density of 1064 kg/m^3 was obtained. Since granule size and the shapes of spray dried TiO_2 and spray dried alumina surface treated TiO_2 were similar, the results reported by Li (2019) suggested that the packing ability of these powders is better when the powder has been coated with higher levels of surface treatments. A possible reason for the better packing ability may be due to a reduction in powder cohesiveness with increasing surface treatment level. In this work, the higher levels of surface treatments may also contribute to a reduction in powder cohesiveness, however it is expected that granule size will be more dominant. In Chapter 5, the influence of surface treatments on powder cohesion is investigated in greater detail.

Powder flowability is often indirectly inferred from bulk and tapped densities through the use of the Hausner ratio, HR which is defined in Equation 4.2 (Hassanpour et al., 2019).

$$HR = \frac{\rho_{tapped}}{\rho_{bulk}} \quad (4.2)$$

The HR is thought to reflect the friction conditions in a moving mass of powder rather than a static situation (Chan and Page, 1997; Abdullah and Geldart, 1999). The HR also provides information regarding the ability of the powder to pack from a loosely packed state to a more highly packed state, thus, eliminating the influence of solid particle density and allowing the influence of powder packing to be considered (Hassanpour et al., 2019).

The HR obtained for SD0.5, SD3.0 and SFD3.5 were found to exhibit similar values of 1.27-1.29, whilst SD3.5 was determined to have a lower value at 1.22. According to Geldart et al. (2006), a drop in the HR is regarded as a decrease in powder cohesion and with most powders, the HR decreases with increasing particle size. Therefore, the lower HR determined for SD3.5 can probably be accounted for by its larger particle size. Since SFD3.5 has the largest granule size, the HR is significantly higher than expected. However, the HR has also been found to increase with a decrease in particle sphericity. Apparently, particles which are more spherical pack better than irregular shaped granules (Abdullah and Geldart, 1999). Therefore, the higher HR for SFD3.5 in comparison to SD3.5 can be accounted for by its irregular particle shapes despite its much larger particle size. Li (2019) has also determined HR values for spray dried alumina coated

TiO₂ featuring buckled granule structures and spherically formed granules structures. The *HR* values were determined to be 1.09 and 1.06 respectively. Therefore, the trends observed in this work are consistent with those reported by others. Additionally, Li (2019) has also observed an increase in *HR* for spray dried TiO₂ in comparison to spray dried alumina surface treated TiO₂. Therefore, the results of Li (2019) suggested that the applied surface treatments can also lead to a lower *HR* and a reduction in cohesion. In this work, cohesion is also expected to reduce for powders containing higher levels of surface treatment, however the influence of size and shape are expected to be more dominant for the same reasons stated previously.

Classification of powder flowability via the *HR* can be classified into six criteria; >1.4 Non flowing, >1.4 Cohesive, 1.25-1.4 Fairly free-flowing, 1-1.25 Free-flowing, 1-1.25 Excellent flowing, 1-1.25 Aerated (Hassanpour et al., 2019). Based upon these criteria, SD0.5, SD3.0 and SFD3.5 were classified as Fairly-free flowing, whilst SD3.5 was identified as Free-flowing.

Table 4.1 - Determined solid, bulk and tapped densities, and Hausner Ratio (*HR*) for spray dried and spin flash dried titanium dioxide.

<i>Powder</i>	<i>Solid density</i> (kg/m ³)	<i>Bulk density (kg/m³)</i>	<i>Tapped density</i> (kg/m ³)	<i>Hausner Ratio</i>
SD0.5	4070 ± 30	791 ± 9	1022 ± 7	1.29
SD3.0	4000 ± 30	846 ± 5	1076 ± 4	1.27
SD3.5	3990 ± 40	927 ± 5	1128 ± 6	1.22
SFD3.5	4010 ± 30	1050 ± 8	1351 ± 5	1.29

4.3.2 FT4 compressibility

Compressibility is a bulk property that reflects the ability of the powder to become consolidated when subjected to a normal stress (Fu et al., 2012). During the FT4 compressibility test, the powder bed is slowly compressed from 1 to 15 kPa with a vented piston to let entrained air escape. This powder compression process involves a reduction in the bulk powder volume and as a result of the applied pressure, the particles are rearranged to form a closer particle packing structure (Mohan, 2012).

Displayed in Figure 4.1 are the results which were obtained during compressibility measurements. For each applied pressure, the compressibility, *C* of the powder was defined as the percentage change in volume after compression, Equation 4.3 (Freeman, 2006);

$$C = \frac{V_i - V_c}{V_i} \times 100\% \quad (4.3)$$

where V_i is the initial volume and V_c is the volume after compression. The results show that the order of compressibility for the supplied powders are $SD0.5 > SD3.0 > SFD3.5 > SD3.5$. These results therefore suggest that SD0.5 is the most compressible powder and the most cohesive, whilst SD3.5 is the least compressible and the least cohesive.

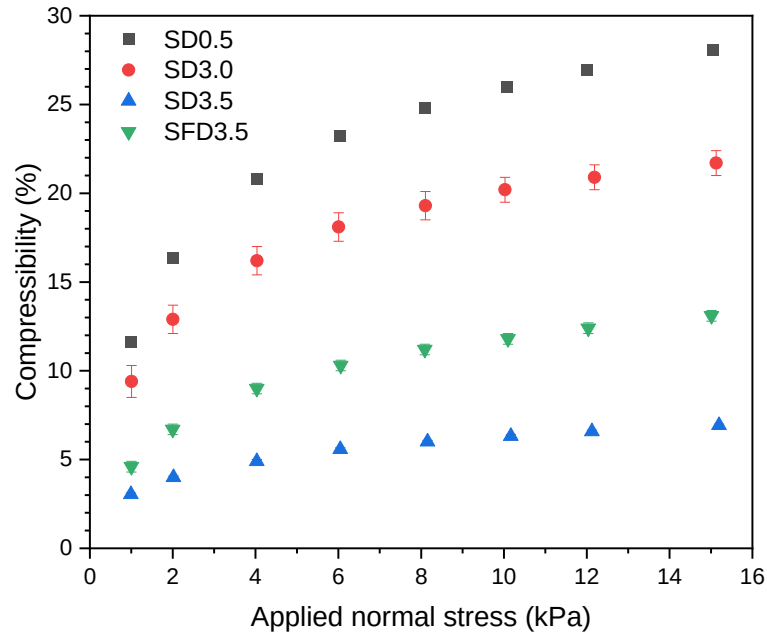


Figure 4.1 - Compressibility data for applied normal stresses of 1 - 15 kPa.

Considering only the spray dried powders, the order of compressibility is $SD0.5 > SD3.0 > SD3.5$. This order is most probably explained by the influence of particle size since these three powders all feature similar shaped particles but different mean particle sizes. SD0.5 has the smallest particle size, whilst SD3.5 has the largest particle size. A powder which has a smaller mean size will be more cohesive and therefore large voids of air will be trapped within the powder increasing its bulk volume. During compression, these voids are easily collapsed allowing the air to escape. Hence, a larger change in volume and a higher compressibility is recorded. Similar trends have been reported by others for a range of particulate solids such as glass beads, aluminium, tungsten powders (Freeman and Fu, 2008), PVC, metal oxides, carbon (Lecturia et al., 2014), spray dried mannitol (Takeuchi et al., 2018) and lactose powders (Fu et al., 2012). All authors reported that powders with larger average particle sizes displayed lower compressibility. Fu et al. (2012) also attributed this trend to the larger particle size which reduced cohesivity and allowed the powder to pack more efficiently.

Despite spin flash dried SFD3.5 having the largest particle size, compressibility measurements showed that this powder is the 2nd least compressible. This result can probably be explained by the influence of its non-spherical particle shape which allows the particles to interlock preventing the powder from packing more efficiently. If SFD3.5, exhibited a spherical particle shape, it would be expected that its compressibility would be much better than SD3.5. Again, the influence of shape has also been reported by others, Fu et al. (2012) for lactose powders and Brika et al. (2020) for gas and plasma atomised Ti-6Al-4 V powders. Likewise, these researchers studied powders with similar mean sizes but different particle shapes. The particles with lower sphericity were shown to have higher compressibility. Both authors attributed their results to the fact that the lower sphericity prevents the powder from packing more efficiently due to the mechanical interlocking effect.

4.3.3 Static angle of repose

For spray dried and spin flash dried titanium dioxide, powder flowability was first directly evaluated using the poured static angle of repose method. During this test, semi-cones of powders were formed against a vertical Perspex wall from a vibrating chute and hopper. The angle of repose, *AoR* was then determined from the maximum height, *h* and the average radius, *r* of the formed semi-cone using Equation 4.1;

$$AoR = \tan^{-1}(h/r) \quad (4.1)$$

For each powder, the determined AoR values can be found listed in Table 4.2. Also listed in this table are the static friction coefficients, which are defined as the force that is required for an object to start sliding (Beakawi Al-Hashemi and Baghabra Al-Amoudi, 2018). The static friction coefficients, μ_s were determined using Equation 4.2;

$$\mu_s = \tan (AoR) \quad (4.2)$$

A larger AoR and hence larger μ_s indicates that the powder is more cohesive and less free-flowing (Geldart et al., 2006; Zhou and Qiu, 2010). This is because a semi-cone is formed with a structure which exhibits a smaller radius and a greater height. For this type of structure to form, the number of contacts and the strength of the interparticle interactions must be greater. Furthermore, the formation of a semi-cone with a smaller radius and greater height will also be promoted by non-spherical particles which are able to interlock.

The values which are listed in Table 4.2 demonstrates that SD0.5 is the most cohesive and the least free-flowing spray dried powder, whilst SD3.5 is the most free-flowing spray dried powder. These results can be explained by the fact that the spray dried powders all exhibit spherical shapes but have different sizes. SD0.5 has the smallest average size, whilst SD3.5 has the largest particle size. It is known that the AoR gradually decreases with increasing mean size because cohesion

decreases (Geldart et al., 2006). Therefore, our results are consistent with those reported by others. A smaller particle size will lead to a greater surface area allowing many more inter-particle contacts to form, which will help to produce a semi-cone with a smaller radius and a taller height, resulting in a larger AoR.

For spray dried titanium dioxide, the strength of the interparticle forces may also be influenced by the applied surface treatments. In the work of Li (2019), AoR measurements were also undertaken on spray dried titanium dioxide. The average particle size of the spherically produced spray dried granules were $\sim 30\text{ }\mu\text{m}$. Li (2019) obtained an AoR of $35 \pm 3^\circ$ for spray dried TiO_2 and an AoR of $31 \pm 2^\circ$ for spray dried alumina coated TiO_2 . These results indicated that an alumina surface treatment could therefore reduce cohesion. Therefore, in this work, a higher level of surface treatment may also contribute to a lower AoR for SD3.0 and SD3.5 in comparison to SD0.5 by reducing the strength of the interparticle forces. However, it is expected that granule size will have a more dominant influence.

Considering spin flash dried SFD3.5, in terms of size and composition, this powder is most similar to SD3.5. The AoR's obtained for these two powders were found to be very similar. SFD3.5 has a larger average particle size which will reduce its AoR, however its irregular granular shapes will promote interparticle locking leading to a semi-cone with a smaller radius and taller height. During AoR tests, for SFD3.5, this will result in a larger AoR which is similar to that of SD3.5. Therefore, under these conditions, it appears that shape has a more dominant influence than particle size on the flowability of SFD3.5. For non-spherical granular shapes, an increase in AoR was also observed by Li (2019) who found that the AoR was larger for spray dried alumina coated TiO_2 featuring buckled granule structures in comparison to spray dried alumina coated TiO_2 featuring spherically formed granules. Therefore, the results reported in this work are consistent with the work of Li (2019).

Powder flowability measured by the AoR can be classified into four criteria; $<30^\circ$ Good powder flowability, $30\text{-}45^\circ$ Some cohesiveness, $45\text{-}55^\circ$ True cohesiveness, $>55^\circ$ Sluggish or Very high cohesiveness (Geldart et al., 2006). According to these four criteria, the powder flowability of the supplied powders are classified as having some cohesiveness. However, SD0.5 lies on the border between some cohesiveness and true cohesiveness.

Table 4.2 - Determined static AoR results and static friction coefficients for supplied spray dried and spin flash dried titanium dioxide powders.

Parameter	SD0.5	SD3.0	SD3.5	SFD3.5
AoR (°)	45 ± 1	43.2 ± 0.6	38.1 ± 0.5	40 ± 1
μ_s	1.00 ± 0.03	0.93 ± 0.03	0.78 ± 0.03	0.84 ± 0.03

4.3.4 Schulze shear cell testing

The results from Schulze shear cell testing are displayed in Figure 4.2 and listed in Table 4.3 are the flow indices obtained for each powder. The flow function plot shown in Figure 4.2 essentially displays a summary of the shear testing results and by plotting the unconfined yield stress versus the major principle stress, enables the average flow index for each powder to be determined from the inverse of the slope. In general, the steeper the slope, the more cohesive the powder (Fitzpatrick et al., 2004). Therefore, as the flow function moves in a clockwise direction towards the major principle stress axis, the better the powder flowability becomes. The greater slope of the flow function line implies that the granules have developed a greater strength upon consolidation, which is then required to be overcome by a greater force to initiate flow.

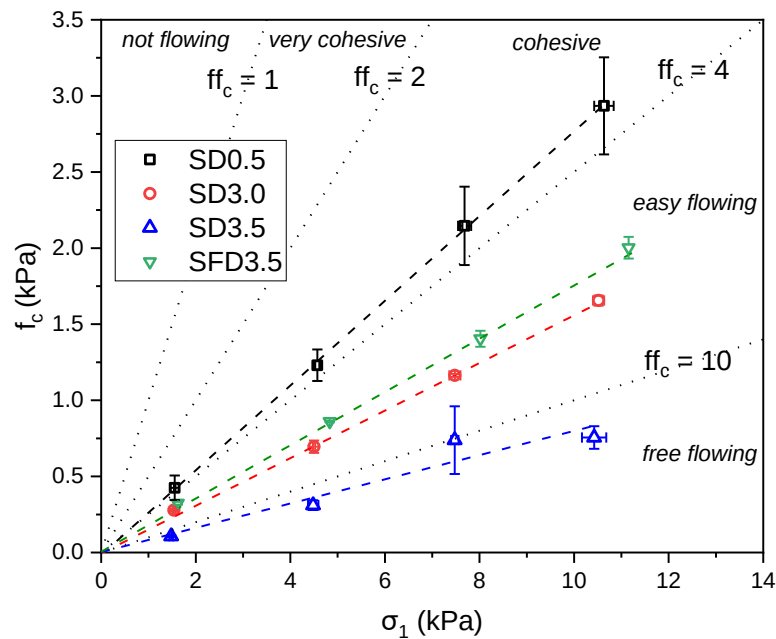


Figure 4.2 - A flow function plot for spray dried and spin flash dried titanium dioxide, where f_c is the unconfined yield strength and σ_1 is the major principle stress. Note: the plot is divided into five regions according to Jenike's classification of powder flowability.

Table 4.3 - Flow indices obtained during Schulze shear cell testing for spray dried and spin flash dried titanium dioxide.

<i>Sample</i>	<i>ffc</i>	<i>R</i> ²	<i>Classification</i>
SD0.5	3.60 ± 0.05	0.9996	Cohesive
SD3.0	6.4 ± 0.3	0.9966	Easy flowing
SD3.5	13 ± 3	0.9088	Free flowing
SFD3.5	5.7 ± 0.2	0.9972	Easy flowing

The flow function plot shown in Figure 4.2 has been divided into five regions according to Jenike's classification of powder flowability via the flow index; <1 not flowing, 1-2 very cohesive, 2-4 cohesive, 4-10 easy flowing and >10 free flowing (Schwedes, 2003). According to Jenike's classification, SD0.5 was classified as cohesive ($ffc = 3.60 \pm 0.05$). In contrast, with a flow index of 13 ± 3 , SD3.5 is classified as free flowing. Situated in the easy flowing regime, SFD3.5 and SD3.0 were determined to have flow indices of 5.7 ± 0.2 and 6.4 ± 0.3 respectively and were therefore classified as easy flowing. Noteworthy, across the applied pre-consolidation stresses, for all four powders, the flow indices were found to remain relatively constant. Considering only the spray dried powders, the ffc order is $SD0.5 < SD3.0 < SD3.5$, which identifies SD3.5 as the most free flowing spray dried powder and SD0.5 as the least free flowing spray dried powder. For reasons stated previously, this trend can more than likely be accounted for by the relative sizes of each powder. SD0.5 was determined to have the smallest particle size, whilst SD3.5 was determined to have the largest granule size for the spray dried powders. For SD0.5 in comparison to SD3.0, since these two powders have relatively similar sizes, it is also likely that the lower level of surface treatment could contribute to its greater cohesiveness, however it is probable that the size has a more dominant effect. In Chapter 5 the effect of surface treatments on powder cohesion is investigated in greater detail. Despite its larger particle size, spin flash dried SFD3.5's powder flowability appears to be impacted by its non-spherical granular shapes, which highlights the dominant influence that shape can have upon the flowability of these materials.

During Quasi-static powder flow characterisation, particle attrition was also considered. After shear cell testing, powder samples were collected and their particle size distributions were determined. Comparison of these distributions against the original particle size distributions showed that no significant changes had occurred, indicating that particle attrition during shear cell testing for all samples did not take place (Figure A4.1).

Additional insights with regards to the influence of a powders characteristics on its Quasi-static flow behaviour can be found by examining the values obtained from individual yield loci. Displayed in Table 4.4 are the parameters obtained from yield loci when a pre-consolidation stress

of 7 kPa was applied. An example of a single yield locus diagram with defined parameters is also displayed in Figure 4.3. During shear testing, each yield locus is analysed using the Mohr-Coulomb failure criterium which relates the shear stress, τ to the applied normal stress, σ and the cohesion parameter, c , Equation 4.5 (Hassanpour et al., 2019);

$$\tau = \mu\sigma + c \quad (4.5)$$

At steady state flow, the properties of the powder can be described by the effective yield locus which has an intercept of 0,0, Equation 4.6 (Schulze, n.d.; Zhou and Qiu, 2010);

$$\tau = \mu_e\sigma \quad (4.6)$$

In Equations 4.5 and 4.6, μ and μ_e are the internal and effective friction coefficients and are related to the internal, ϕ_i and effective internal angles of friction, ϕ_e via Equations 4.7 and 4.8;

$$\mu = \tan \phi_i \quad (4.7)$$

$$\mu_e = \tan \phi_e \quad (4.8)$$

ϕ_i and ϕ_e provide a measure of the internal friction between particles at static and steady state flow respectively (Farshchi, 2018).

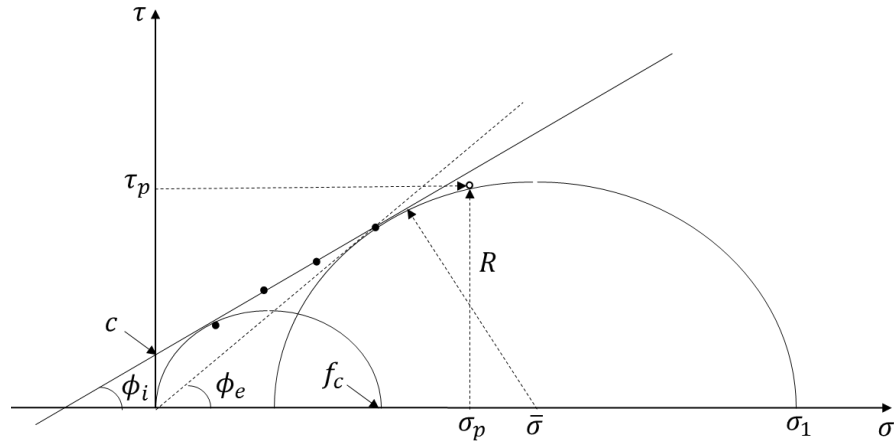


Figure 4.3 - An example of a yield locus plot displaying defined parameters and constants. The yield locus plot also displays the yield locus (linear solid line) and the effective (linearized) yield locus (linear dashed line). Yield locus plot was redrawn from Hassanpour et al. (2019).

It must be recalled here, that during the quasi-static flow regime, particle interactions occur via frictional sliding and therefore ϕ_i and ϕ_e are important parameters to be considered. For the powders under study, the internal angles of friction were found to follow the order of

SFD3.5=SD0.5>SD3.0>SD3.5, which reflects the level of friction experienced by each powder during shear.

In terms of composition and particle size, SFD3.5 is most similar to SD3.5. Despite SFD3.5 having a larger particle size, the higher level of friction determined for SFD3.5 can be accounted for by its non-spherical and irregular shaped granules. In fact, several authors have reported that the internal friction angle increases with increasing particle angularity (Yousuff and Page, 1993; Podczec and Miah, 1996; Chan and Page, 1997; Shinohara et al., 2000; Zegzulka et al., 2018). According to Shinohara et al. (2000), the increase in interparticle friction for irregular shaped particles is owed to the interlocking effect.

All spray dried granules have been shown to display relatively spherical granules and the magnitude of the internal angles of friction have been shown to follow the order of SD0.5>SD3.0>SD3.5. To account for this trend, again the influence of size is considered. Podczec and Miah (1996) have found that the internal friction angle decreases with an increase in particle size. These findings are probably due to the fact that particle surface area decreases with increasing particle size, which reduces contact area in the particle bulk assembly leading to a reduction in friction

The term c has the dimensions of stress, is termed the cohesion parameter and represents the stress required to break the attractive interparticle forces in order to initiate shear powder flow (Hassanpour et al., 2019). The obtained values of c for the supplied powders were found to follow the order of SD0.5>SFD3.5>SD3.0>SD3.5. These results therefore suggested that SD0.5 is the most cohesive, whilst SD3.5 is the least cohesive. Considering only the spray dried powders, the order of c for these powders is SD0.5>SD3.0>SD3.5, which again reflects their relative cohesiveness due to size. The greater value of c obtained for SFD3.5 in comparison to SD3.5 can be attributed to the non-spherical and irregular granular shapes, where a higher shear stress is required to overcome the interlocking of its granules.

Table 4.4 – Parameters obtained from shear cell testing of spray dried and spin flash dried titanium dioxide when a pre-consolidation stress (σ_p) of 7 kPa was applied.

<i>Sample</i>	ϕ_i (°)	c (Pa)	ϕ_e (°)
SD0.5	28 ± 1	889 ± 85	34 ± 2
SD3.0	26.5 ± 0.4	508 ± 11	29.8 ± 0.4
SD3.5	24.9 ± 0.5	234 ± 23	27.0 ± 0.5
SFD3.5	30 ± 1	572 ± 5	34 ± 1

4.3.5 FT4 stability and variable flow rate

The FT4 powder rheometer consists of a blade which rotates around a vertical axis whilst moving downwards and then upwards through a pre-conditioned powder bed. During a downward or upward motion of the blade, the torque, T and axial force, F_{ax} on the blade is measured as a function of height, H . In doing so, the rotational, ω and downward velocity, v_{ax} of the blade is kept constant. The total input work done on the blade during one of these motions is reported as the total flow energy, E_f , Equation 4.9 (Hassanpour et al., 2019);

$$E_f = \int_0^H \left(\frac{T\omega}{v_{ax}} + F_{ax} \right) dH \quad (4.9)$$

The stability and variable flow rate test program is actually two tests methods in one program which first measures the stability of the powder at a specific flow rate and then variable flow rate conditions. The test program consists of 11 test cycles, the first 7 of which constitutes the stability program and are undertaken at a blade tip speed of 100 mm/s. Following these 7 test cycles, a further 4 test cycles are undertaken at blade tip speeds of 100, 70, 40 and 10 mm/s and make up what is known as the variable flow rate test. The stability and variable flow rate program characterises five characteristics of any powder, which are 1) the conditioned bulk density, 2) the basic flow energy, 3) specific flow energy, 4) powder bed stability and 5) the variable flow rate. The results from the stability and variable flow rate test can be found presented in Figure 4.4 and Table 4.5.

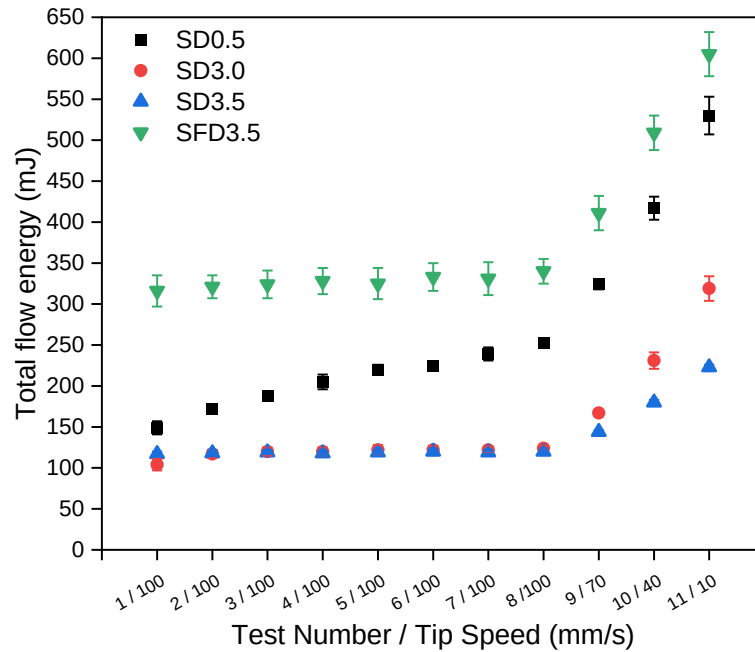


Figure 4.4— FT4 powder rheology stability and variable flow rate test results.

Table 4.5— Determined parameters obtained during the FT4 stability program (Test numbers 1 – 7).

Sample	SD0.5	SD3.0	SD3.5	SFD3.5
<i>CBD (kg/m³)</i>	870 ± 10	892 ± 3	1000 ± 2	1090 ± 10
<i>E_{BF} (mJ)</i>	239 ± 8	122 ± 4	119 ± 2	331 ± 20
<i>E_{nBF} (mJ/g)</i>	11.0 ± 0.4	5.5 ± 0.2	4.8 ± 0.1	12.2 ± 0.6
<i>E_{SF} (mJ/g)</i>	7.8 ± 0.3	6.2 ± 0.3	3.86 ± 0.07	6.4 ± 0.1
<i>SI</i>	1.6 ± 0.1	1.17 ± 0.05	1.02 ± 0.03	1.05 ± 0.02
<i>FRI</i>	-	2.58 ± 0.06	1.86 ± 0.02	1.78 ± 0.06

The conditioned bulk density (CBD) is determined from the pre-conditioned and split sample mass, and the split sample cell volume. The obtained CBD's can be found tabulated in Table 4.5 and were found to be consistent with obtained poured bulk densities and hence a similar trend was also observed. However, the reproducibility's of some CBD's in contrast to the poured bulk densities were slightly better. The better reproducibility of CBD's can be attributed to the fact that the CBD is operator independent and much better reproducible packing states can be formed (Freeman, 2008a).

The Basic Flow Energy (BFE) is calculated from the work done in moving the blade through the powder from the top of the vessel to the bottom. The flow pattern established is a downward anti-clockwise motion of the blade. During this motion, the powder is pushed forwards and downwards in front of the blade in a confined environment generating a compressive and relatively high stress mode in the powder. The BFE, E_{BF} is recorded in the seventh repetition of the stability and variable flow rate program, Equation 4.10 (Freeman, 2013b; Brika et al., 2020).

$$E_{BF} = E_{f,Test\ 7\downarrow} \quad (4.10)$$

The E_{BF} can also be expressed as the normalised Basic Flow Energy (E_{nBF}) where it is normalised by dividing the E_{BF} by the split sample mass, m , Equation 4.11;

$$E_{nBF} = \frac{E_{f,Test\ 7\downarrow}}{m} \quad (4.11)$$

E_{BF} and E_{nBF} can be found reported in Table 4.5. The obtained flow energies for all seven test cycles of the stability part of the stability and variable flow rate test program are also graphically displayed in Figure 4.4.

According to Freeman (2013), the BFE can be quite complex to interpret as the BFE is dependent on many physical properties. A low BFE represents a powder with good flow properties and a high BFE, a powder that will flow poorly. However, the opposite can also be true, where powders

that flow freely under gravity result in a high BFE and powders that are cohesive, a low BFE. Which therefore makes the ranking of powder flowability via the BFE not possible.

Despite this, several trends have been observed between powder properties and the BFE which can be useful for understanding dynamic powder flow. One of these trends is the influence of particle size and bulk density on the BFE. Generally, larger particles and higher bulk densities result in a larger BFE (Lu et al., 2023). Two studies in particular which have reported this trend are the works of Lu et al. (2023) and Du et al. (2023). Lu et al. (2023) studied powders with sizes between 7.38 – 119.84 μm and Du et al. (2023) with powders of sizes between 0.03 – 27.40 μm . Both authors found that the BFE increased with larger particle sizes and higher bulk densities. According to Freeman (2013b), this can be explained by the fact that powders consisting of larger particles are less cohesive, affected more by gravity and pack more efficiently. When flow is induced in this type of powder, the flow zone is transmitted far ahead of the blade and hence a larger BFE is recorded. In contrast, powders consisting of smaller particles are more cohesive and tend to contain pockets of air and hence their bulk density is lower. When flow is induced in this type of powder, the resulting flow or stress transmission zone is relatively localised and the displaced powder volume is small. Hence, the determined flow energy is also small. Fine cohesive powders are also known for their affinity to agglomerate and form clusters (Ku et al., 2015). These agglomerates and clusters can also create additional resistance to the FT4's blade, leading to a much higher BFE being measured.

Another trend is the influence of particle shape, where non-spherical and irregular shaped particles are found to increase the BFE. For example, Nan et al. (2017) experimentally and theoretically analysed the powder rheometry of the FT4 and the effect of particle shape on the flow energy. Their results showed that the flow energy required for agitating a bed of rodlike particles was much larger than that of spheres. Using radio frequency plasma spheroidization, Wang et al. (2016) prepared spherical AlSi10Mg powders from an irregular shaped powder feedstock. After dynamic testing, the prepared spherical powders were found to have a much lower BFE value. The potential for irregular shaped particles to interlock, increasing interparticle friction, which creates more resistance to the FT4's blade is likely to account for these observations.

Freeman (2013) also states that if the difference between powder samples is due to surface texture or flow additive, then a reduction in the BFE can also be observed. For example, Mangal et al. (2016) demonstrated that coating paracetamol particles with increasing amounts of spray dried polyvinylpyrrolidone-leucine particles led to a reduction in the BFE. The spray dried polyvinylpyrrolidone-leucine particles were found to act as guest particles which adhered to the surface of the paracetamol particles, reducing cohesion and improving flowability. A second

study undertaken by Goh et al. (2021) showed that coating α -lactose monohydrate powders with different amounts of magnesium stearate from 0.2 – 5 wt% also led to reduction in the BFE. Magnesium stearate is known to modify the surface characteristics of a powder, act as lubricant, reducing van der Waal force interactions and thereby promoting powder flow. These studies therefore suggested that the flow additives reduce cohesion, which therefore creates less resistance to the FT4's blade resulting in a lower BFE being recorded.

Considering the results which were obtained for spray dried and spin flash dried titanium dioxide, it is apparent that the spin flash dried material exhibited the highest BFE, which can be explained by the fact that it has the largest particle size and the highest bulk density. Furthermore, its irregular granular shapes are also expected to contribute to its much higher BFE. The BFE trend observed for the spray dried powders was found to be SD0.5>SD3.0>SD3.5. Since, this BFE trend does not correlate with particle size and bulk density, the influence of the applied surface treatments must be considered. The surface treatment levels applied to SD0.5, SD3.0 and SD3.5 are 0.5, 3.0 and 3.5 wt% respectively. Therefore, it appears that under the conditions tested, the surface treatments are acting to reduce interparticle cohesion in a similar way to flow additives. The mechanism by which the surface treatments reduce cohesion is investigated and reported in Chapter 5.

The Specific Flow Energy (SFE) is calculated from the work done in moving the blade through the powder from the bottom of the vessel to the top (Freeman, 2008b). Therefore, during measurement of the SFE, the flow conditions in which the powder experiences is entirely different in comparison to the BFE. The flow pattern which is established during measurement of the SFE is an upward clockwise motion of the blade, which generates gentle lifting and subjects the powder to flow in a low stress unconfined environment. The SFE is therefore a measure of how easily a powder will flow in an unconfined or low stress environment. The SFE, E_{SF} is obtained from an average of the Test 6 and Test 7 flow energies during the upward clockwise motion of the blade from the powder bed and is then normalised against the split mass, Equation 4.12 (Freeman, 2008b);

$$E_{SF} = \frac{E_{f, \text{Test 6}} + E_{f, \text{Test 7}}}{2m} \quad (4.12)$$

According to Freeman (2008), due to the low stress environment, cohesion is often the most influential property and as a general rule, the more cohesive the powder is, then the higher the SFE will be. As the SFE does not depend upon powder density, it is much better than the BFE for ranking powders for their flowability (Fu et al., 2012). With regards to powder properties, powders with smaller sizes and irregular shapes have been found to result in larger SFE values (Fu et al., 2012). Furthermore, lubricants such as magnesium stearate which adhere and coat particle surfaces have also been shown to reduce the SFE (Zhou et al., 2010; Goh et al., 2021).

Therefore, larger particle sizes and surface coatings will reduce cohesion, whilst irregular shaped particles will lead to an increase in friction due to particles interlocking.

The SFE for the spray dried powders were ranked in the order of SD0.5>SD3.0>SD3.5. Again this order is the same order obtained for the AoR and the flow function. The BFE results showed that the surface treatments were the most dominant factor which influenced powder flow during the downward motion of the blade, however as the flow conditions in the upward motion of the blade differs, it is difficult to say whether this still remains the case for the SFE. However, it is expected that a larger size and a higher surface treatment level will both contribute to a reduction in cohesion, which will therefore reduce the resistance experienced by the blade. With regards to spin flash dried SFD3.5, this powder was determined to be the 2nd most cohesive sample and is most likely due to its irregular shaped granules which interlock increasing the resistance experienced by the blade, resulting in a higher SFE being measured.

According to Freeman (2008), powder flowability measured by the SFE can be classified into one of three criteria; <5 mJ/g Low cohesion, 5 – 10 mJ/g Moderate cohesion, >10 mJ/g High cohesion. Based upon these three criteria, SD0.5, SD3.0 and SFD3.5 were identified as having moderate cohesion and SD3.5 was classified as having low cohesion.

The stability of a powder bed is assessed by applying the same test conditions to a powder over seven test cycles and observing if any changes occur. Powder bed stability is also assessed via the stability index, *SI* which is defined as the ratio of the flow energy of Test 7 to the flow energy of Test 1, Equation 4.13 (Freeman, 2010).

$$SI = \frac{E_{f,Test\ 7\downarrow}}{E_{f,Test\ 1\downarrow}} \quad (4.13)$$

The assessment of powder bed stability provides an indication as to whether the powder is changing during defined conditions and a set time period. An *SI* of ~1 is said to be stable, whereas an *SI* lower or greater than 1 is said to be unstable (Freeman, 2010; Jüptner and Scherließ, 2020).

As mentioned previously, test cycles 1 – 7 are performed at the same tip speed of 100 mm/s to assess the stability of the powder sample during dynamic flow conditions. During these 7 test cycles, the total flow energies for SD3.5, SFD3.5 and SD3.0 stay relatively constant indicating stable powder beds. Though it must be noted here, that SD3.0 also shows some initial instability between test cycles 1 and 2. This slight instability is reflected in its *SI*, which has a value of 1.17 ± 0.05 . However, in comparison to SD0.5, the instability of SD3.0 is minor. The *SI*'s for SD3.5 and SFD3.5 were also determined to be 1.02 ± 0.03 and 1.05 ± 0.02 respectively, indicating that these powders have stable powder beds. In contrast, the stability behaviour of SD0.5 differs from the other three powders. Instead, a gradual increase in total flow energies from 110 to 150 mJ is

observed between test cycles 1 – 7. Its stability index was also determined at 1.6 ± 0.1 indicating an unstable/changing powder bed. According to Freeman (2010), when the $SI > 1$, possible causes of powder bed instability can be due to de-aeration, agglomeration, segregation, moisture uptake and electrostatic charge. In Chapter 3, the moisture sorption characteristics of SD0.5 was investigated. Therefore, moisture sorption is unlikely to be the cause. The DVS isotherms showed the moisture content of the powder changes very little under the conditions of the tests. Electrostatic charge is also unlikely to be the cause. In Chapter 5, the influence of electrostatics on powder cohesion is considered. Since SD0.5 is very cohesive, segregation is also very unlikely to be the cause. Size segregation usually occurs in free-flowing powders where the gravitational forces are more dominant than cohesive forces (Tang and Puri, 2004). Instead the instability of SD0.5 can be accounted for by de-aeration and agglomeration. According to Freeman (2010), de-aeration usually occurs in cohesive powders with low bulk density. It must be recalled here that during bulk, tapped and conditioned bulk density tests, SD0.5 was determined to have the lowest density, which is consistent. Because the particles are packed inefficiently, the powder bed contains a high proportion of air and when made to flow, the air is squeezed from the bulk. The agitation of the powder bed also encourages agglomerates to form. The formation of agglomerates leads to an increase in the particle packing efficiency and particle size. As a consequence, the bulk density is increased leading to more particle-particle shearing which creates increased resistance to the FT4's blade. The overall effect leads to an increase in the flow energies with increasing test cycle number. Similar observations have also been reported by Jüptner and Scherließ (2020). Further evidence to support the instability of SD0.5 can be found in the blade height versus force profiles displayed in Figure A4.2. From these profiles, values of the measured force at a height of 15 mm were extracted from each profile for each test number. Figure 4.5 displays the extracted data from these profiles, where the measured force at a bed height of 15 mm is plotted versus test number. For SD3.0, SD3.5 and SFD3.5, the measured force stays relatively constant throughout the stability test indicating the bed is stable. In contrast, the measured force for SD0.5 shows a gradual increase throughout the stability test. This indicates that over time, going from test to test, the mass of powder in front of the blade is gradually increasing and further suggests that the powder bed is densifying.

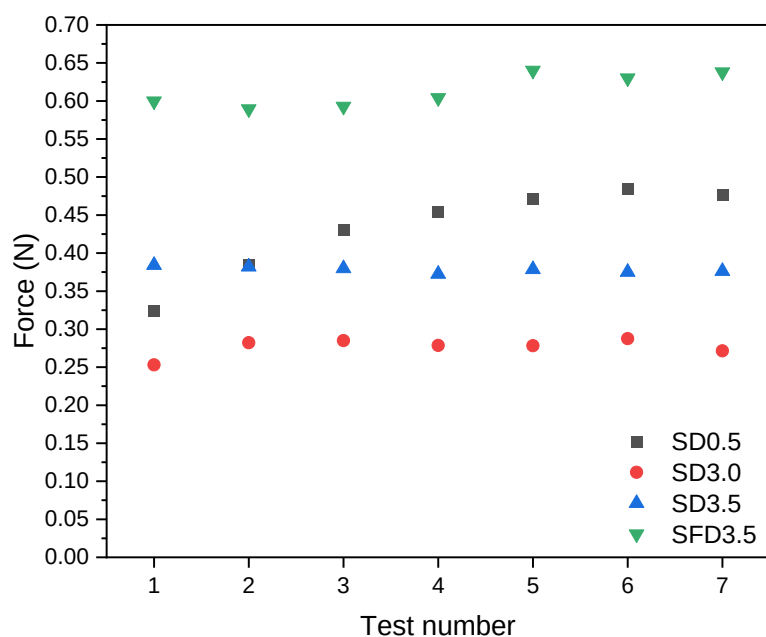


Figure 4.5 - Blade force (measured at a height of 15 mm) versus test number. Very little change in the measured force as a function of test number indicates a stable powder bed, whilst an increase indicates instability.

The rate at which powders are handled and moved through a given process will vary. Even the most basic transfer systems will require the powder to flow at reduced rates in some locations and at higher flow rates in other places (Freeman, 2007). Therefore, a powders sensitivity to varying flow rate conditions is an important parameter to measure. It must also be noted here, that the variable flow rate test is only undertaken on powders which have been shown to be stable during the stability test. Otherwise, the data obtained is a combination of a powders instability, as well as its response to changing flow rates, which therefore makes data interpretation difficult (Freeman, 2007). Since SD0.5 was shown to be unstable during the stability test, it's *FRI* is not reported here and is therefore excluded from the following discussions.

In Figure 4.4, test cycles 8 – 11 are the results which were obtained from the variable flow rate test program. It must be recalled here that during test cycles 8 – 11, the blade tip speed is gradually reduced from 100 to 10 mm/s. For all four powders analysed by this method, it can be seen that the flow energy increases. According to Freeman (2007), at higher flow rates, the powder is agitated more by the blade and in doing so increases its air content. The greater volume of air in the powder also acts as lubricant reducing the number of interparticle contacts and therefore decreases the measured flow energies. At low flow rates, the powder bed is more consolidated and therefore, the measured flow energies are higher. By analogy to fluid rheometry, the variable

flow rate test essentially studies the influence of shear rate upon a powders viscosity. As the blade tip speed (shear rate) is reduced, the measured total flow energies (the powders viscosity) decreases for our materials. These results therefore suggest that the supplied powders behave in a similar manner to a shear thinning fluid upon the application of increasing strain rates.

For comparative purposes, the sensitivity of a powder to changing flow rate conditions is assessed via the Flow Rate Index (*FRI*) which is defined as the ratio of the E_f obtained during Test 11 to the E_f obtained during Test 8, Equation 4.14 (Freeman, 2007; Ludwig and Miller, 2015).

$$FRI = \frac{E_{f,Test\ 11}}{E_{f,Test\ 8}} \quad (4.14)$$

The *FRI* of the supplied powders were found to lie between 1.78 - 2.58. According to Freeman (2007), powder flowability via the *FRI* can be classified into one of four criteria; <1 Pseudoplastic or Newtonian flow rate, ~1 Flow rate insensitive, 1.5-3 Average flow rate sensitivity, >3 High flow rate sensitivity. Therefore, according to this classification system, the supplied powders were identified as having average flow rate sensitivity to changing flow rate conditions.

The *FRI* of our powders were also found to follow the order of SD3.0>SD3.5>SFD3.5. A higher *FRI* indicates the powder is more sensitive to changing flow rates and is more cohesive. This is because during agitation, a cohesive powder is able to entrain more air within the powder bed in comparison to a non-cohesive powder. Therefore, for a cohesive powder, a larger difference between the flow energies are measured at the highest and lowest tip speeds (Freeman, 2007). The obtained *FRI* order for our materials therefore shows that SD3.0 is the most sensitive and SFD3.5 is the least sensitive to changing flow rate conditions. Under the test conditions, this order also shows that SD3.0 is the most cohesive, whilst SFD3.5 is the least cohesive of these three powders.

4.3.6 FT4 aeration

The bulk flow properties of powders can be affected by air content, which can influence how the particles interact (Freeman, 2013a). Therefore, it is important to understand how a powders air content influences its powder flow properties. The aeration test program of the FT4 powder rheometer quantifies the sensitivity to aeration which provides value in understanding how powders behave when the process introduces air to the powder and in other environments where flow under gravity is important (Freeman, 2013a).

The aeration program measures flow energies over 7 test cycles. During the first test cycle, air is not introduced into the powder column and the flow energy is measured. After the first test cycle, air is then introduced into the powder column at a specific air velocity to evaluate the flow energy

of the powder at different air contents (or air velocities). During the experiments, the flow energies for the supplied powders were measured at air velocities of 0, 2, 4, 6, 8 and 10 mm/s.

Displayed in Figure 4.6 and tabulated in Table 4.6 is the aeration data which was obtained using the standard aeration program of the FT4 powder rheometer. The graph in Figure 4.6 shows that as the aeration velocity is increased from 0 – 10 mm/s, the flow energies decrease and then plateau's for all four powders. When the flow energy plateau's, this indicates that the powder has become fully fluidised, i.e. the powder has become completely aerated (Cordts and Steckel, 2012). The data displayed in Figure 4.6, shows that all powders become fully fluidised at air velocities greater than 8 mm/s.

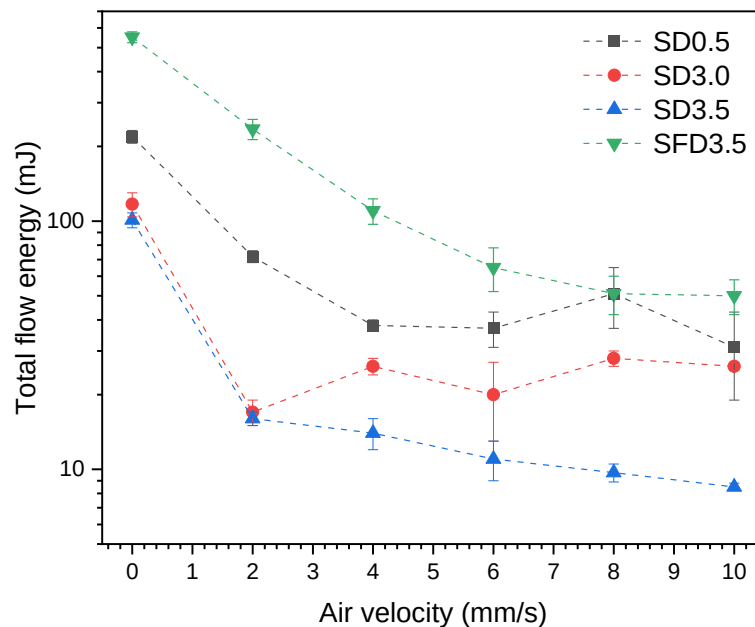


Figure 4.6 – Aeration data for spray dried and spin flash dried titanium dioxide at air velocities of 0 – 10 mm/s.

At all air velocities, the flow energies obtained for the spray dried powders were found to follow the order of $SD0.5 > SD3.0 > SD3.5$ and this order was found to correlate with the relative cohesiveness of these three powders, which is a result of size and surface treatment level (See stability and variable flow rate discussion). When air is passed through the powder bed, the particles become separated, the bed volume expands, the bulk density of the powder becomes lower and hence the measured flow energy is also lower. For a powder which is more cohesive, complete separation of the particles is prohibited and the air channels through the powder bulk (Freeman, 2013a; Lefebvre et al., 2020). Hence, for a specific air velocity, the flow energy

remains higher for a more cohesive powder, which explains why the flow energy is higher for SD0.5 and lower for SD3.5.

Consistent with the stability and variable flow rate data, the flow energies of SFD3.5 for each air speed are larger than the other three powders. Since this powder is non-cohesive, the flow energy of this powder can be attributed to its much larger particle size, higher bulk density and irregular particle shape (See stability and variable flow rate discussion). With increasing air velocities, this powder was also found to behave in a similar manner to the spray dried powders, i.e. with increasing air velocities, the flow energies decreased and then plateaued.

The sensitivity of a powder to aeration can be quantified by the Aeration Ratio, AR which is a ratio of the BFE , i.e the flow energy when no air is introduced, to the flow energy at an air velocity of 10 mm/s, AE_{10} . This ratio of flow energies is given in Equation 4.15;

$$AR_{10} = \frac{BFE}{AE_{10}} \quad (4.15)$$

A benefit of assessing the aeration sensitivity of a series of powders by using the AE_{10} is due to the fact that the influence of sample mass is eliminated allowing better comparisons to be made (Cordts and Steckel, 2012). According to Freeman (2013), a powder which has an $AR \sim 1$ is not sensitive to aeration, a powder which has an AR between 2 – 20 has average sensitivity to aeration, whilst a powder which has an $AR > 20$ is very sensitive to aeration. Therefore, based upon these criteria and the AR_{10} values listed in Table 4.6 suggests that the supplied powders all display average sensitivity to aeration. Furthermore, the AR_{10} values listed in Table 4.6 suggests that all powders have similar aeration sensitivity and therefore these results also indicate that the ability of the powders to aerate is unlikely to be influential to bulk powder handling during conveying.

Table 4.6 – Aeration results for spray dried and spin flash dried titanium dioxide.

Powder	BFE (mJ)	AE_{10} (mJ)	AR_{10}
SD0.5	219 ± 13	31 ± 12	9 ± 5
SD3.0	117 ± 13	26 ± 1	4.4 ± 0.5
SD3.5	101 ± 7	8.5 ± 0.3	12 ± 1
SFD3.5	551 ± 28	50 ± 8	11 ± 2

4.3.6 Flow regime classification for the FT4 powder rheometer

A characteristic of the dynamic powder flow regimes (intermediate and rapid granular) is the presence of a stress-strain relationship (Tardos et al., 2003). As previously mentioned, Hare and Ghadiri (2017) have analysed the stress and strain rate of the FT4 powder rheometer and their results have suggested that the FT4 powder rheometer is capable of operating in the intermediate/dynamic flow regime. Therefore, based upon the work of Hare and Ghadiri (2017), in this study, the dimensionless strain rates have been estimated for our materials to determine the potential flow regimes in which our experiments may be operating in. The strain rates, γ were calculated via Equation 4.16;

$$\gamma = dv/(n_{band}d_p) \quad (4.16)$$

where dv is the velocity differential across the shear band ($0.9v_{tip}$), n_{band} is the number of particles in the shear band, which was estimated at 5 and d_p is the average particle diameter. The dimensionless strain rate, γ^0 was calculated using Equation 4.17;

$$\gamma^0 = \gamma\sqrt{d_p/g} \quad (4.17)$$

where g is the acceleration due to gravity. Equations 4.16 and 4.17 show the importance of estimating the dimensionless strain rate as they are in fact material specific and therefore despite employing the same experimental conditions, the flow regime assessed may vary from one powder to another. Our estimations of the strain rates can be found listed in Table 4.6, where the flow regimes have been classified according to Tardos et al. (2003). For the spray dried powders, our estimates suggest that the FT4 operates within the intermediate flow regime for tip speeds of 100, 70 and 40 mm/s and in the Quasi-static flow regime at tip speeds of 10 mm/s. For the spin flash dried material, our estimates advocate that the FT4 operates in the intermediate flow regime at tip speeds of 100 and 70 mm/s and in the Quasi-static flow regime at tip speeds of 40 and 10 mm/s. However, since Hare and Ghadiri (2017) stated that the shear band may increase for fine cohesive powders due to clustering and that further work would be needed to investigate this, for our estimations, this must also be held in mind.

Table 4.7 - Estimated dimensionless shear rates and classification of flow regimes. Estimations were based upon an $n_{band} = 5$ and the $D[v,0.5]$ particle size.

<i>Powder</i>	<i>Impeller tip speed (mm/s)</i>	<i>Shear rate (s^{-1})</i>	<i>Dimensionless strain rate</i>	<i>Flow regime</i>
SD0.5	100	367	0.82	Intermediate
	70	257	0.57	Intermediate
	40	147	0.33	Intermediate
	10	37	0.08	Quasi-static
SD3.0	100	333	0.78	Intermediate
	70	233	0.55	Intermediate
	40	133	0.31	Intermediate
	10	33	0.08	Quasi-static
SD3.5	100	250	0.68	Intermediate
	70	175	0.47	Intermediate
	40	100	0.27	Intermediate
	10	25	0.07	Quasi-static
SFD3.5	100	105	0.44	Intermediate
	70	73	0.31	Intermediate
	40	42	0.18	Quasi-static
	10	10	0.04	Quasi-static

Since it is known that the torque measured on the FT4's blade accounts for approximately 85% of the measured flow energy (Nan et al., 2021), further evidence to support the fact that the FT4 is operating in the dynamic flow regimes can be found by examining the blade torque versus height profiles for test cycles 8 – 11. The torque versus height profiles are shown in Figure A4.3, which shows torque variations as a function of height. From these profiles, the torque measured at a height of 15 mm were extracted and are shown as a function of tip speed in Figure 4.6. These plots highlight the fact that stress-strain relationships are present, or otherwise the tip speed (applied strain) would have no influence on the measured blade torque (stress).

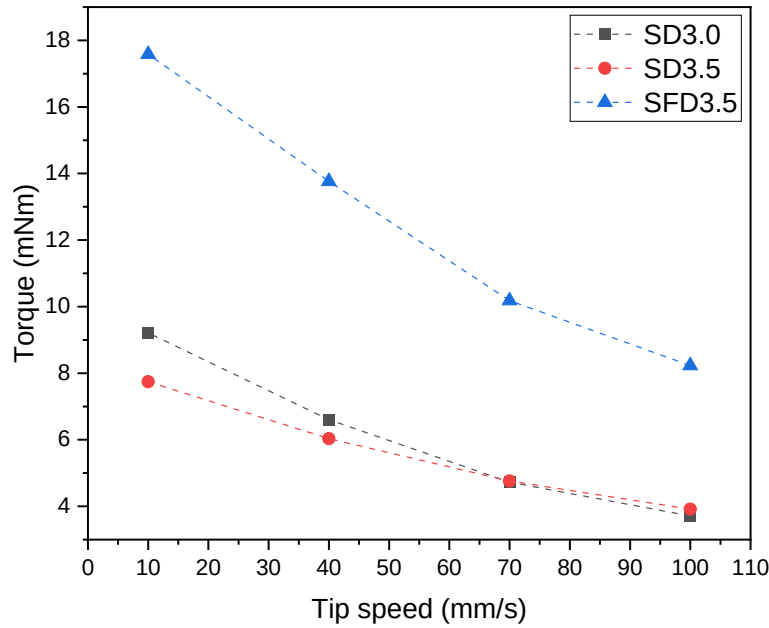


Figure 4.7 - Blade torque (measured at a height of 15 mm) versus tip speed for SD3.0, SD3.5 and SFD3.5. The data shows evidence of stress-strain relationships.

4.4 Conclusions

In bulk solids handling, good powder flow characteristics are vital in order for a given powder to be transported between unit operations. Therefore in this chapter, spray dried and spin flash dried titanium dioxide powders were subjected to a number of tests in order to study their bulk flow behaviour. These tests were bulk and tapped densities, FT4 compressibility, static angle of repose, Schulze shear cell, the FT4 stability and variable flow rate and FT4 aeration testing. Tapped density and compressibility tests were employed to study how the solid fraction of the supplied powders varied under tapping and under deformation, whilst the angle of repose and Schulze shear cell and FT4 dynamic flow test was used to subject the powders to a range of flow conditions and study their flow behaviour. Moreover, the flow regimes in which the FT4 powder rheometer operated in for our materials was determined. Overall, these six tests have subjected the supplied powders to a range of conditions, which have included pouring, tapping, deformation, shearing, agitation and aeration. Furthermore, these six tests have utilised a range of methods and metrics to evaluate and rank the powder flowability for the supplied materials. In this study, the flow regimes in which the selected powder flow characterisation techniques operated in were also considered. The static AoR, Schulze shear cell and FT4 powder rheometer was therefore used to evaluate powder flow in the static, Quasi-static and intermediate flow regimes respectively. Hence

when combined, these results provide a comprehensive picture for the flowability of spray dried and spin flash dried titanium dioxide.

The powder flowability of the spray dried powders were found to be governed by their size and surface treatment level. A smaller particle size and lower surface treatment level was found to increase cohesion. An increase in powder cohesion was therefore found to entrain air, reduce bulk density and increase compressibility. During powder flow tests, a greater cohesiveness was also found to produce taller structures in the static flow regime, increase friction in the Quasi-static flow regime and increase resistance to induced flow in the dynamic flow regime. A greater cohesiveness also enabled the powder to develop a much greater strength when consolidated which was highlighted via the flow function and furthermore resulted in an unstable powder bed which was demonstrated by the stability index. Overall, for spray dried titanium dioxide, better powder flowability was observed for powders which were less cohesive, i.e. powders containing larger particles and higher surface treatment levels.

As for spin flash dried SFD3.5, the flowability of this material was dominated by its larger particle sizes and irregular shaped granules. Bulk densities and packing was improved by its larger particle size, however its non-spherical granular shapes were found to increase its compressibility. Despite its larger particle size, the irregular shaped granules were found to increase friction via mechanical interlocking in all flow regimes, which therefore significantly impacted the flowability of this material.

Overall, this study has shown that titanium dioxide granules which are larger, more spherical with higher levels of surface treatments will be less cohesive and display much better powder flowability. Furthermore, this study has also developed a relationship between powder behaviour at the process scale to the lab scale testing, which means that these results can be used to predict the bulk handling characteristics of potential spray dried or spin flash dried titanium dioxide materials in the future.

Chapter 5 – Adhesion and cohesion

5.1 Introduction

During bulk powder handling, the adhesion and cohesion of fine particles can cause undesirable effects such as unpredictable or unreliable flow and blockages (Zafar et al., 2014). Adhesion is the physical phenomena by which two different materials stick together, whereas cohesion is the adherence of two surfaces composed of the same material. Adhesion and cohesion arise from the various interparticle forces and is known to be affected by surface topography. To develop our overall understanding of the bulk handling behaviour of spray dried and spin flash dried titanium dioxide, in this chapter we investigate adhesion and cohesion.

In general, adhesion/cohesion forces between particles to surfaces or to other particles come as a result of capillary, electrostatic, and van der Waals forces (Petean and Aguiar, 2015), and can be influenced by the physicochemical properties of the materials which are in contact and the environmental conditions (Salazar-Banda et al., 2007; Petean and Aguiar, 2015). Therefore for any adhesion study, these factors must be held in mind.

The attractive capillary forces form between particles when they are in close proximity and the powder absorbs water vapour at its surfaces. Eventually, a liquid phase builds-up and capillary menisci form between the particles creating an attractive force (Tselishchev and Val'tsifer, 2003). The capillary force is at least 1 or 2 orders of magnitude higher than the van der Waals force (Afrassiabian et al., 2016). An increase in relative humidity generally increases particle adhesion, and according to Podczec et al. (1997), when the relative humidity of the air is above 65%, the capillary forces can dominate above all other forces.

Electrostatic forces often arise by tribo-electrification which is the acquisition of electrostatic charges due to interparticle friction or collisions between particles. These charges are known to create attractive or repulsive forces depending on their sign (Hassanpour et al., 2019). In a humid environment, the electrostatic attraction can be reduced to zero due to a de-charging of the system (Visser, 1989).

Occurring between all atoms and molecules, the van der Waal forces are interaction forces which always exist, are short range and arise between permanent or induced electric dipoles (Hassanpour et al., 2019). When these electric dipole moments are close together and become correlated, they give rise to an attractive force (Leite et al., 2012).

The roughness of a surface can play an important role in adhesion since it can reduce the contact area between particles. Generally, experiments and modelling suggest an increase in surface roughness leads to a reduction in the adhesion force (Israelachvili, 2011). In fact, roughness can

change the van der Waals force by up to several orders of magnitude (Castellanos, 2005). Surfaces may possess roughness in several length scales, but due to the short range of the van der Waals interaction, roughness in nanoscale ultimately determines the strength of adhesion (Katainen et al., 2006). Surface roughness can also complicate adhesion measurements due to the fact that the true contact area is always an unknown quantity (Hooton et al., 2003). The presence of molecular absorbed water is also known to affect the van der Waal forces. The mere presence of a thin layer of liquid, even if it is no more than a monolayer, can change the adhesive interaction between two bodies considerably (Leite et al., 2012).

To the best of our knowledge, the only work which has investigated the adhesion of titanium dioxide pigment is the work of Jones et al. (2003). Using Atomic Force Microscopy (AFM), Jones et al. (2003) investigated the adhesion of four titania powders; two alumina coated rutile samples and two uncoated anatase powders, all with a particle size of 0.2 μm . Whilst not stated, the 0.2 μm size suggested that these titania powders may have also been micronized. The particles were mounted onto cantilevers and force-distance measurements were undertaken. The force-distance curves were not found to be of a simple form, but were similar for all four materials. The non-simple form was attributed to the compression and rearrangement of fine particles. The force-distance curves also showed very little relative humidity (RH) dependence (range studied was 10 - 90% RH) and there was little evidence for long range electrostatic forces. These findings therefore suggested that the adhesive behaviour observed was most likely due to the van der Waal forces.

Reported in Chapter 3, it was shown that the powders under study adsorbed relatively little moisture (<1 wt% at 40%RH) and capillary menisci were not detected during SEM analysis. Moreover, the ratio of moisture content to surface area for all four powders were found to be similar. Therefore, these findings support the fact that the amount of any moisture present would likely to have an equal influence on the adhesive behaviour for each powder and overall these results suggested that the observed adhesive behaviours is unlikely to be due to capillary forces.

Considering the influence of electrostatics, it is known that for fine neutral powders, the electrostatic force is negligible compared to the van der Waals force (Castellanos, 2005). In fact the electrostatic force is known to be approximately 10 times smaller than the van der Waals force (Petean and Aguiar, 2015). Furthermore, once adhesion has taken place, the electrostatic force becomes less significant, and other forces such as the van der Waals are known to become more important (Debrincat et al., 2008). Therefore, from these discussions and from the work of Jones et al. (2003), it can deduced that the level of adhesion observed for the four samples studied in this work are most likely to be due to the van der Waal forces.

Experimentally, adhesion and cohesion are investigated using two main techniques, particle detachment methods such as the drop test or the centrifuge method (Salazar-Banda et al., 2007) and AFM. In this work, the particle detachment method was used to determine the relative adhesiveness of the supplied samples. The particle detachment method involves the dispersion of a powder sample on to a substrate followed by subjecting the particles to a detachment force. Since particle size, geometry and surface roughness can vary for a polydispered powder sample, an average adhesion force can be obtained (Salazar-Banda et al., 2007). AFM was then employed to understand the contributions of the surface roughness and the surface chemistry to the adhesion. In fact, a wealth of information was provided from the AFM which included, surface topography, roughness, height and adhesion maps. Thus in this work, the drop test has been utilised to investigate the overall adhesion of our samples, whilst the AFM has been used to study the contributions of the surface roughness and the surface chemistry to the overall adhesion.

Review of adhesion theory

The total adhesion force between two particles or a particle and a surface, F_{ad} can be assumed to be the sum of several forces, Equation 5.1;

$$F_{ad} = F_c + F_{es} + F_{vdw} \quad (5.1)$$

where F_c is the capillary force, F_{es} is the electrostatic force and F_{vdw} is the van der Waals force (Salazar-Banda et al., 2007). If the adhesion is solely due to the van der Waal forces, then Equation 5.1 can be rewritten as Equation 5.2.

$$F_{ad} = F_{vdw} \quad (5.2)$$

Van der Waal's is a general name given to describe three forces with different origins. These forces are known as Keesom, Debye and London forces (Leite et al., 2012). Keesom forces are permanent dipole-permanent dipole interactions and occur between the permanent dipoles of polar molecules (Leite et al., 2012). Debye forces (also known as induction or polarisation forces) are permanent dipole-induced dipole interactions. They arise when a permanent dipole temporally distorts an electron cloud of a non-polar molecule. Subsequently, an induced dipole is formed leading to an attractive interaction (Leite et al., 2012). London forces (also known as dispersion forces) are interactions which arise between instantaneous dipole-induced dipoles. London forces are attractive forces which operate between all atoms and molecules (Butt et al., 2005; Leite et al., 2012), whereas Keesom and Debye forces require permanent dipoles (Leite et al., 2012).

In 1937, Hamaker developed the theory of van der Waal's between macroscopic bodies (Leite et al., 2012). According to Hamaker's law, the van der Waals force between two equal sized spherical particles can be estimated using Equation 5.3;

$$F_{vdw} = \frac{A_H R}{12z_0^2} \quad (5.3)$$

where R is the particle radius, z_0 is the shortest distance between the particle surfaces and A_H is the Hamaker constant, which quantifies the atom-atom pair van der Waals interaction (Spillmann et al., 2008). The van der Waals force between two particles is therefore a summation of all the individual atomic and molecular interactions (French, 2000).

The work of adhesion, W_{ad} is defined by the negative of the Gibbs free energy change per unit area of the interacting interfaces and is expressed by the Dupré equation, Equation 5.4 (Salazar-Banda et al., 2007; Israelachvili, 2011);

$$W_{ad} = \gamma_1 + \gamma_2 - \gamma_{12} \quad (5.4)$$

where γ_1 and γ_2 is the surface energy of surface 1 and surface 2 and γ_{12} is the surface energy of surface 1 in contact with surface 2. The materials of surfaces 1 and 2 also differ. When the two surfaces are made from the same composition the work of adhesion becomes the work of cohesion, i.e $W_{ad} = W_c$ and Equation 5.4 becomes Equation 5.5, since $\gamma_{12} = 0$.

$$W_c = 2\gamma \quad (5.5)$$

Equation 5.4 and Equation 5.5, demonstrate that the surface energies of the materials have an important role to play in adhesion and cohesion. The surface energy represents the effects of the van der Waal forces of a material on itself, effectively a self-energy, producing a surface tension at the interface between the material and the gas phase (French, 2000).

The adhesion force, F_{ad} between a particle and a surface can also be expressed as Equation 5.6 which is also known as JKR theory (Johnson et al., 1971);

$$F_{ad} = \frac{3}{2}\pi R W_{ad} \quad (5.6)$$

In Equation 5.6, the work of adhesion is also known as the interfacial surface energy.

Israelachvili (2011) also shows that the work of adhesion is proportional to the Hamaker constant, since Equations 5.2, 5.3 and 5.6 can be combined to give Equation 5.7;

$$W_{ad} = A_H/12\pi z_0^2 \quad (5.7)$$

These equations therefore demonstrate the relationships between the adhesion force, the work of adhesion, surface energy, van der Waal forces, the Hamaker constant and hence the surface chemistry. Since the models discussed rely upon perfectly smooth spheres, it must also be recalled here that surface roughness influences the magnitude of adhesion or cohesion by affecting the contact area between particles. This means that for adhesion/cohesion influenced by van der Waal

forces, the two main factors which will be influential are (1) the surface roughness and (2) the surface chemistry.

5.2 Materials and methods

5.2.1 Drop test

Particle adhesion force measurements were undertaken using the drop test method reviewed by Zafar et al. (2014). During these experiments, samples were dispersed onto an aluminium sample stub which is then subjected to a vertical drop down a Perspex tube. At the end of the vertical drop, the sample stub impacts at the stopper base and due to their inertia, the particles experience a tensile force. Due to the balance of the particle adhesion and detachment forces, a critical particle size is determined where particles which are smaller remain adhered to the stub and where particles which are larger are detached from the stub. By utilising high speed imaging to record the stubs deceleration on impact and by applying JKR theory and Newton's second law of motion, the detachment forces are determined and then used to calculate particle interface energies and adhesion forces. There are several aspects to this method which include the drop test setup/apparatus, high speed imaging, sample dispersion, image analysis, sample preparation and test conditions. In the sections which follow, these aspects are discussed in more detail.

Drop test apparatus

The vertical drop of the sample stub (diameter 16 mm) is undertaken using a Perspex tube with an internal diameter of 20 mm and a length of ~200 mm. The Perspex tube is attached to the bottom of a Perspex box with a hole (stopper base) which has an internal diameter of 12 mm. Before the drop, the sample stub is attached to a metal screw (length ~55 mm) which acts as a stabiliser keeping the sample stub in position for impact. The drop test apparatus used during the particle adhesion method is displayed in Figure 5.1.

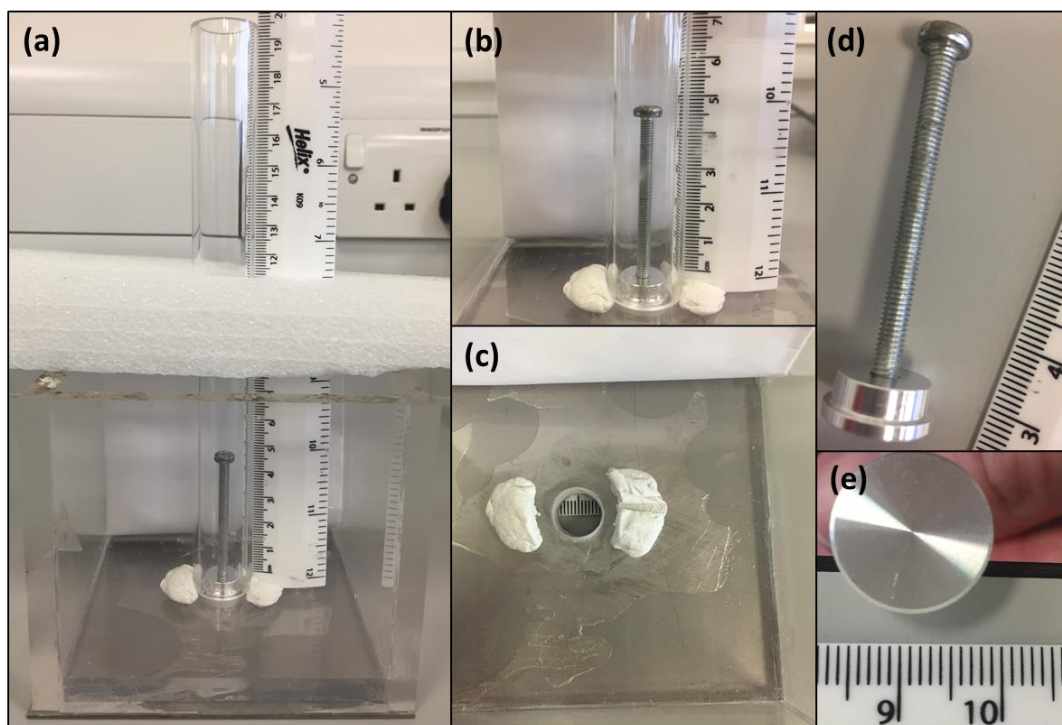


Figure 5.1 - Drop test apparatus and accessories which were used to measure particle adhesion forces and interface energies. (a) Drop test set-up with drop tube, (b) close up of sample stub inside the drop tube (c) stopper base (d) sample stub with stabiliser and (e) sample stub displaying the face in which the sample is dispersed on.

High speed imaging

The drop of the sample stub is recorded using a Photron Fastcam SA5 high speed video camera. From the high speed imaging, the pictures are analysed to determine the stubs impact velocity and the stubs contact time with the stopper. The drops were recorded with a frame capture rate of 75,000 fps and images were obtained with a resolution of 256 x 128 pixels. During high speed imaging, the last 15 mm of the drop is imaged so that impact velocities and contact times can be determined.

Sample dispersion

The dispersion of the particles onto the sample stub is undertaken using the Malvern Morphologi G3. Using low energy dispersion settings (0.5 bar injection pressure, 20 ms injection time and 60 s settling time), $\sim 15 \text{ mm}^3$ of powder is dispersed by the G3's dispersion unit. During this dispersion process, a small portion of this sample is deposited on to the sample stub. After dispersion, the sample stub is inverted to allow any loose particles not adhered to the sample stub to detach.

Image analysis

The critical particle size is determined by imaging the sample stub before and after the drop using the Malvern Morphologi G3. Afterwards, the obtained images were analysed using ImageJ software to measure the size of particles adhered to the stub before and after impact. The images were captured using a lens with a magnification of 20x and images were obtained with a resolution of 2584 x 2023 pixels. Before dispersing particles onto the stub, the surface of the stub is cleaned with isopropanol to remove any unwanted grease and dust etc. Since the aluminium sample stub contains defects from the machining process, reference images of the sample stub with no particles attached is obtained so that during particle size measurements, particles can be distinguished from stub surface defects. In total, 4 areas of the stub are imaged to increase the numbers of particles measured. The centre of the stub is identified by locating the circular artefact from the machining process. Once located, 4 images of the stub are collected, top left, top right, bottom left and bottom right. This means that during a single analysis, a total of 12 images are collected; 4 reference images, 4 images of particles dispersed onto the stub before impact and 4 images of particles which have remained adhered to the stub after impact.

Sample preparation and drop test conditions

Samples were prepared by passing the powder samples through a sieve with a 63 μm aperture and material <63 μm were collected and used for adhesion measurements. Sieving was undertaken using a powder mass of 15.01 g, over a period of 20 min, interval time of 1 s and an amplitude of 0.5 mm.

Sample dispersion and drop tests were undertaken at a laboratory temperature of $21 \pm 2^\circ\text{C}$ and a relative humidity of $43 \pm 5\%$.

5.2.2 Atomic Force Microscopy

To study the surface topography of the spray dried samples, a Bruker Multimode 8 and a Bruker Icon Fast Scan Bio Atomic Force Microscopes (AFM) were employed. Both AFM's were equipped with Nanoscope 5 controllers and Bruker fast scan A probes. To acquire the 3D topographic maps, both AFM's were operated in Tapping Mode (TM) and images were collected with a scan size of 6 μm . To process the AFM images, a 2nd order plane fit was applied to the 3D surface to correct for surface tilting. Power density spectral profiles were computed using the Nanoscope Analysis 1.9 software by selecting the 2D Isotropic PSD function and then displaying the profile as a 2D Iso plot type.

To study surface adhesion, a Bruker Multimode 8 AFM equipped with a Nanoscope 5 controller operated in Peak Force Tapping (PFT) mode was employed. The AFM was equipped with a Bruker TESPA-150-30 probe, which had a spring constant of 6.095 N/m and a tip material

composed of silicon with a tip radius of 30.8 nm. Height and adhesion data were then collected over a scan size of 2 μm .

To prepare powder samples for analysis, samples were glued to magnetic sample stubs using epoxy resin and then sprayed with compressed air to remove any loose non-attached sample.

5.3 Results and discussion

5.3.1 Particle adhesion

In this work, particle adhesion has been investigated using the drop test method reviewed by Zafar et al. (2014). As described in the methodology section, this test essentially determines the critical particle size at which particles of various sizes detach and remain adhered to the sample stub when subjected to a tensile force via a vertical drop. During the drop tests, an impact velocity, contact time and critical diameter is obtained for each test. These parameters are unique to each test and are used to estimate the adhesive/detachment forces and interface energies. Replicate drop tests are undertaken for each sample and the reported adhesive/detachment forces and interface energies are therefore averages, the error of which is determined from the standard deviation of the replicates. Before moving on to discuss particle adhesion/detachment forces and interface energies, we first review the data obtained from the high speed imaging process (impact velocities and contact times) and data from the determined critical diameters.

Impact velocities and contact times

During tests, each sample is subjected to near identical drop test conditions, i.e, the sample stub and height at which the sample stub is dropped remains the same. Through the use of high speed imaging of the vertical drop of the sample stub, the obtained images were analysed to obtain the stubs impact velocities and contact times. Examples of the images obtained via high speed imaging are displayed in Figure 5.2.

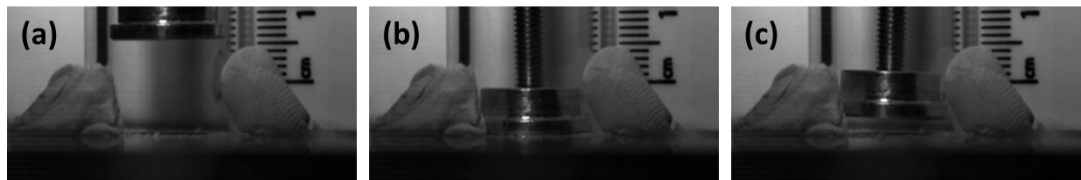


Figure 5.2 - Images obtained from the high speed imaging process of the sample stub (a) before impact (b) at impact and (c) after impact/during rebound.

From 18 drops, the average impact velocity and contact time were determined to be 1.65 ± 0.06 m/s and 0.6 ± 0.1 ms respectively and were deemed to show good reproducibility. The stubs impact force, F was estimated using Equation 5.8;

$$F = \frac{\rho}{0.5t_c} = m_s \frac{v}{0.5t_c} \quad (5.8)$$

where ρ is the momentum of the sample stub, m_s is the stubs mass including stabiliser (6.8605 g), v is the impact velocity and t_c is the contact time. The average stub impact force was found to be 36 ± 6 kN.

Since the potential energy, E_p (Equation 5.9) of an object held at height, h is equal to the kinetic energy, E_k (Equation 5.10) the impact velocity, V of the falling object can be estimated using Equation 5.11;

$$E_p = mgh \quad (5.9)$$

$$E_k = \frac{1}{2}mV^2 \quad (5.10)$$

$$V = \sqrt{2gh} \quad (5.11)$$

where m and g is the mass of the object and the acceleration due to gravity. For a drop height of 0.2 m, the impact velocity of the sample stub can be estimated to have a value of 1.98 m/s. This value is slightly larger than the experimentally determined impact velocity of 1.65 m/s. This difference can be attributed to the fact that during the drop, the sample stub experiences contact with the wall of the drop tube which slows the fall of the sample stub. Air drag and air displacement may also play as factors in resulting in a slighter slower fall. Therefore, the experimentally determined and estimated values of the impact velocity can be considered to be in good agreement.

Critical diameter

To determine the critical diameter, image analysis is used to analyse particles which have adhered to and detached from the sample stub. The critical diameter is defined as the particle size at which less than, particles remain adhered to the sample stub and which above, particles are detached from the sample stub. Figure 5.3 displays examples of images obtained during each experiment. During this analysis three types of particles are identified by blue, green and red circles. Figure 5.3a displays an image of the sample stub before the drop and after dispersing the particles on to the stub. Figure 5.3b displays particles which have remained adhered to the stub after impact and Figure 5.3c displays the reference image which is taken before dispersion. The reference image is utilised to discriminate particles from stub surface defects which are obtained during the machining process (i.e. during the manufacture of the aluminium stub). During the image analysis,

particles which have detached (blue circles) and particles which have remained adhered (green circles) are identified and indexed. The size of these particles were then measured. Moreover, during the image analysis, particles which are present in Figure 5.3b and absent from Figure 5.3a identified by red circles are assumed to be particles which have moved or are particles which have re-attached after the drop. In either case, the adhesive contact between particle and stub has been separated and during the analysis, these particles are disregarded. For a particle to be considered as being adhered to the sample stub, it must also be present in the same location before impact.

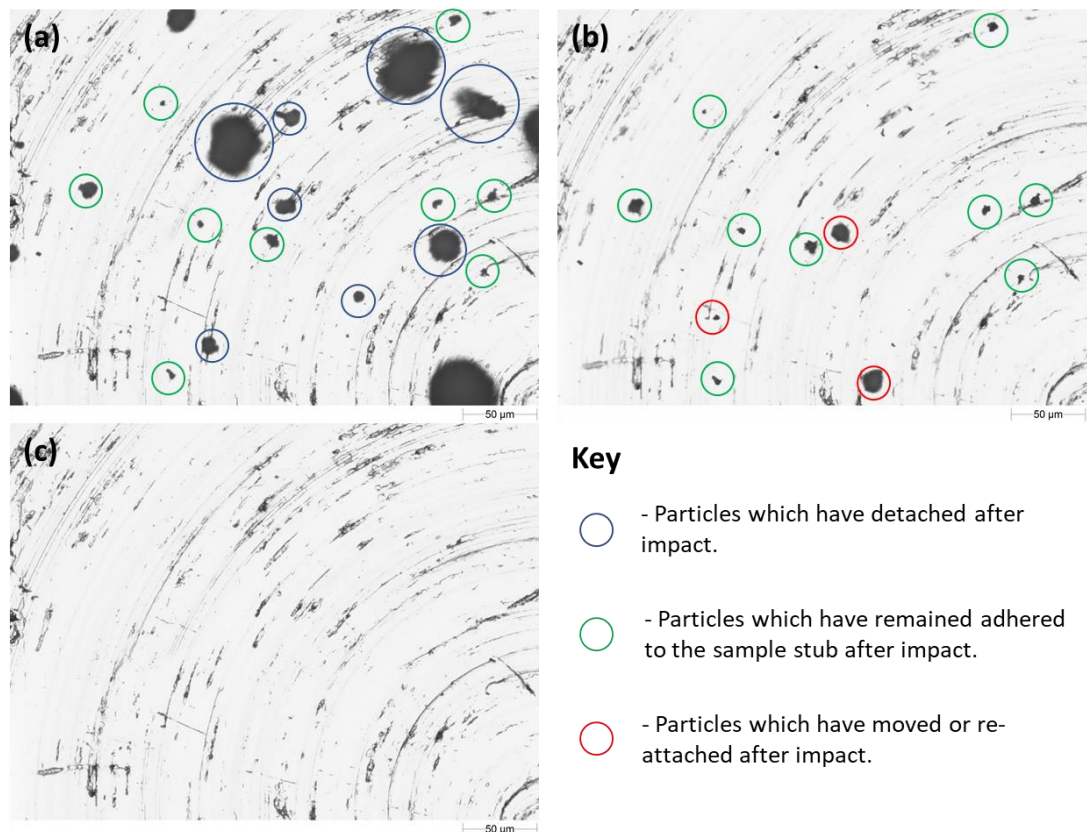


Figure 5.3 - Examples of images collected from the surface of the sample stub (a) before drop (a) after the drop and (c) before dispersion (Reference image). Displayed in the images are also examples of particles which have been identified as detached particles (blue circles), particles which have remained adhered to the stub after impact (green circles) and particles which are disregarded from the analysis (red circles).

Table 5.1 provides some data regarding the average numbers of particles before and after impact from the drop tests. The average number of particles measured before and after impact were ≥ 95 and ≥ 54 particles respectively. This constitutes a particle detachment loss between 35 - 64%. Since sufficient quantities of particles are measured before and after impact, the drop height and tensile force generated during impact is therefore appropriate for the level of particle adhesion displayed by these four materials, i.e, sufficient quantities of particles must remain adhered to the

sample stub after impact in order for measurements to be undertaken and to properly determine the critical diameter.

Table 5.1 – Average numbers of particles measured before and after impact using image analysis.

<i>Parameter</i>	<i>SD0.5</i>	<i>SD3.0</i>	<i>SD3.5</i>	<i>SFD3.5</i>
Average no. particles before	116 ± 64	172 ± 60	179 ± 16	95 ± 26
Average no. particles after	80 ± 56	112 ± 41	64 ± 16	54 ± 19
No. of particles lost (%)	35 ± 13	35 ± 6	64 ± 8	44 ± 5

Once the size of detached and adhered particles had been determined, the particles were then organised into 40 size classes between 1-50 µm. The number of particles detached in each size class is then determined and a particle loss versus particle size curve is obtained. An efficiency loss model, Equation 5.12 (Dirgo and Leith, 1985) was then fitted to the particle loss-particle size curve using non-linear regression to determine the diameter at which 50% of the particles remain adhered to the sample stub and at which 50% of the particles are lost from the stub on impact ($d_{50\%}$);

$$\eta = \frac{1}{1+(d/d_{50\%})^{-b}} \quad (5.12)$$

where η is the number of particles lost from each size class, d is the maximum particle size of the size class and b is a constant. In this work, the $d_{50\%}$ is also equal to the critical diameter, $d_{crit.}$. The critical diameters obtained for each formulation are listed in Table 5.1. An example of a particle loss versus particle size curve with fitted efficacy loss model is provided in Figure 5.4. The particle loss efficiency curve identifies a window where particles remain attached and are lost. Within the particle loss window, some data scatter is observed from the efficiency loss model. Since it is known that surface roughness can cause pull-off force data to scatter (Tormoen et al., 2005), the data scatter in the particle loss window is therefore probably due to the fact that the contact area between the particle and stub can vary due to various levels of surface roughness, but also due to variations in shape and surface chemistry. Due to the statistics of determining the critical diameter, the critical particle diameter represents a particle with a typical/average geometry, surface roughness and surface chemistry.

In this work, the organisation of particles in to size classes and the application of an efficiency loss model, Equation 5.12 is where the methodology of determining the critical diameter differs from the work of Zafar et al. (2014). The methodology described here was found to be more appropriate when determining the critical diameter from a much larger population of particles,

whereas the methodology reported by Zafar et al. (2014) could be more suitable for a smaller population.

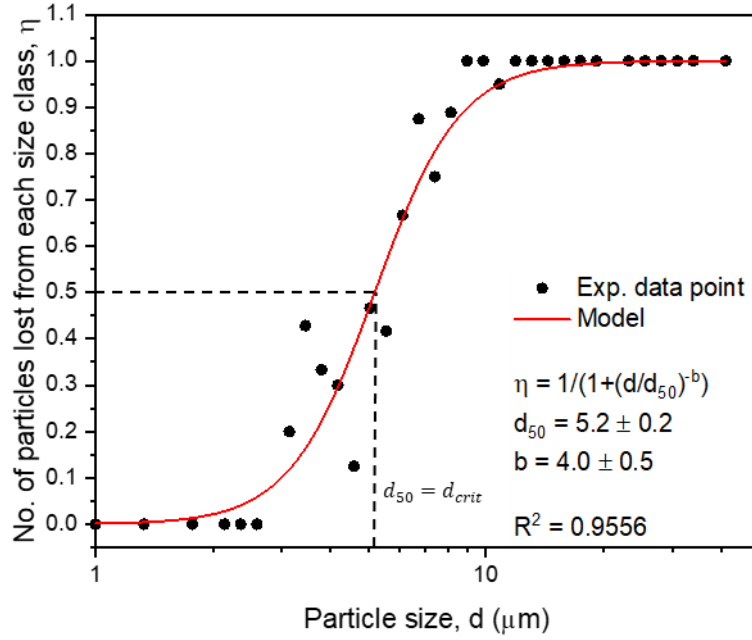


Figure 5.4 - An example of a particle efficiency loss curve which is used to obtain the critical particle diameter during a single drop test measurement.

Estimation of particle detachment/adhesion forces and interface energies

Once values were obtained for the impact velocity, contact time and critical diameter, Newton's 2nd law of motion and JKR theory was then used to estimate particle detachment forces, particle adhesion forces and particle interface energies.

Using Newton's 2nd law of motion, the particle detachment force, F_{det} was calculated using Equation 5.13;

$$F_{det} = \frac{m_p v}{0.5 t_c} \quad (5.13)$$

where m_p is the particle mass, which is estimated from the particle solid density, ρ and the volume of a sphere with the same diameter as the critical particle diameter, d_{crit} . (Equation 5.14);

$$m_p = \rho \times \frac{4}{3} \pi (d_{crit}/2)^3 \quad (5.14)$$

A modified form of the JKR model was then used to calculate the work of adhesion, W_A (Equation 5.15);

$$F_{ad} = \frac{3}{2}\pi(d_{crit.}/2)W_{ad} \quad (5.15)$$

where F_{ad} is the particle adhesion force. The concept of the work of adhesion was discussed earlier in more detail in Section 5.1.

Since particle geometries deviate from perfectly smooth spheres, the interface energy is considered as an apparent surface energy. Due to the method of determining the critical diameter, the critical particle diameter represents a particle with a typical geometry, average surface roughness and surface chemistry. Table 5.2 provides tabulated data for the critical diameter, interface energies and detachment/adhesion forces measured for the supplied powders.

To test whether or not the drop test results were significantly different, a single factor ANOVA (Analysis of Variance) analysis was performed on the detachment/adhesion forces and apparent surface energy data sets for all four samples. The ANOVA analysis determined that the null hypothesis was void indicating that the results were significantly different.

To test the data further, a second ANOVA was performed on SD3.0, SD3.5 and SFD3.5 results. The 2nd ANOVA analysis determined that the null hypothesis was retained, which showed that the SD3.0, SD3.5 and SFD3.5 results were not significantly different. Overall the ANOVA analysis showed that the SD0.5 was significantly different from the other three powders, however SD3.0, SD3.5 and SFD3.5 were not significantly different from each other.

These results show that the order of adhesion for the supplied powders is SD0.5>(SD3.0=SFD3.5=SD3.5) and demonstrates that SD0.5 is the most adhesive powder, whilst SD3.0, SD3.5 and SFD3.5 are the least adhesive powders. For SD0.5, the obtained critical diameters show that the larger particles are retained on the surface of the sample stub after impact, demonstrating that this formulation produces the most adhesive powder of the four materials. In contrast, the smaller critical diameters determined for SD3.0, SD3.5 and SFD3.5 shows that these formulations produce the least adhesive powders. If a powder is more adhesive then it is also likely to be more cohesive, therefore these findings are also important for understanding powder cohesion.

Table 5.2 - Critical particle diameters, apparent surface energies and adhesion forces estimated from drop test data (Particle adhesion force experiment).

<i>Parameter</i>	<i>SD0.5</i>	<i>SD3.0</i>	<i>SD3.5</i>	<i>SFD3.5</i>
Critical diameter, $d_{crit.}$ (μm)	7.8 ± 0.3	5.8 ± 0.7	4.7 ± 0.5	5.8 ± 0.3
Apparent surface energies, W_{ad} (μJ/m ²)	268 ± 4	192 ± 58	100 ± 30	160 ± 30
Adhesion force, F_{ad} (nN)	4.9 ± 0.2	3 ± 1	1.1 ± 0.4	2.2 ± 0.5

5.3.2 Surface topography and surface adhesion

Atomic Force Microscopy (AFM) was employed to further understand the adhesion of the supplied samples. Two different types of experiments were performed, with each experiment being used to investigate different aspects. Tapping Mode (TM) analysis was utilised to investigate the surface topography of the granules, with a particular focus on understanding the surface roughness of the supplied samples. Whilst, Peak Force Tapping (PFT) experiments were used to probe the surface adhesiveness of the samples and hence investigate the influence of surface composition on the adhesion. In comparison to the drop test, the PFT experiments are less influenced by surface roughness and therefore allow the source of adhesion which is related to the surface chemistry and hence the applied surface treatments to be studied. It should be noted here that during the AFM analysis, due to experimental complications, data could not be collected for spin flash dried SFD3.5 and only the spray dried samples could be studied. Therefore, in the sections that follow, the TM and PFT experiments only discuss data obtained for the spray dried samples.

Surface topography

AFM in Tapping Mode was applied to survey the surface of spray dried titanium dioxide. Examples of the three-dimensional topographic maps obtained during this analysis are displayed in Figure 5.5. The 3D topographies visually show that the surface of the spray dried TiO₂ granules all have a similar surface topography. The obtained images are also consistent with the images obtained from the SEM analysis which can be found reported in Chapter 3.

In order to quantitatively assess the surface roughness of the supplied samples, the surface roughness was analysed using two commonly employed roughness metrics and Power Spectral Density (PSD).

The surface roughness of the obtained 6 µm scan sizes were firstly assessed using the Root Mean Square Roughness (Rq) and the Arithmetic Average Roughness (Ra) metrics, (Bruker, n.d.). Rq is the root mean square average of the height deviations taken from the mean image data plane and is expressed in Equation 5.16;

$$Rq = \sqrt{\frac{\sum z_i^2}{N}} \quad (5.16)$$

Whilst, Ra is the arithmetic average of the absolute values of the surface height deviations measured from the mean plane and is defined by Equation 5.17;

$$Ra = \frac{1}{N} \sum_{j=1}^N |Z_j| \quad (5.17)$$

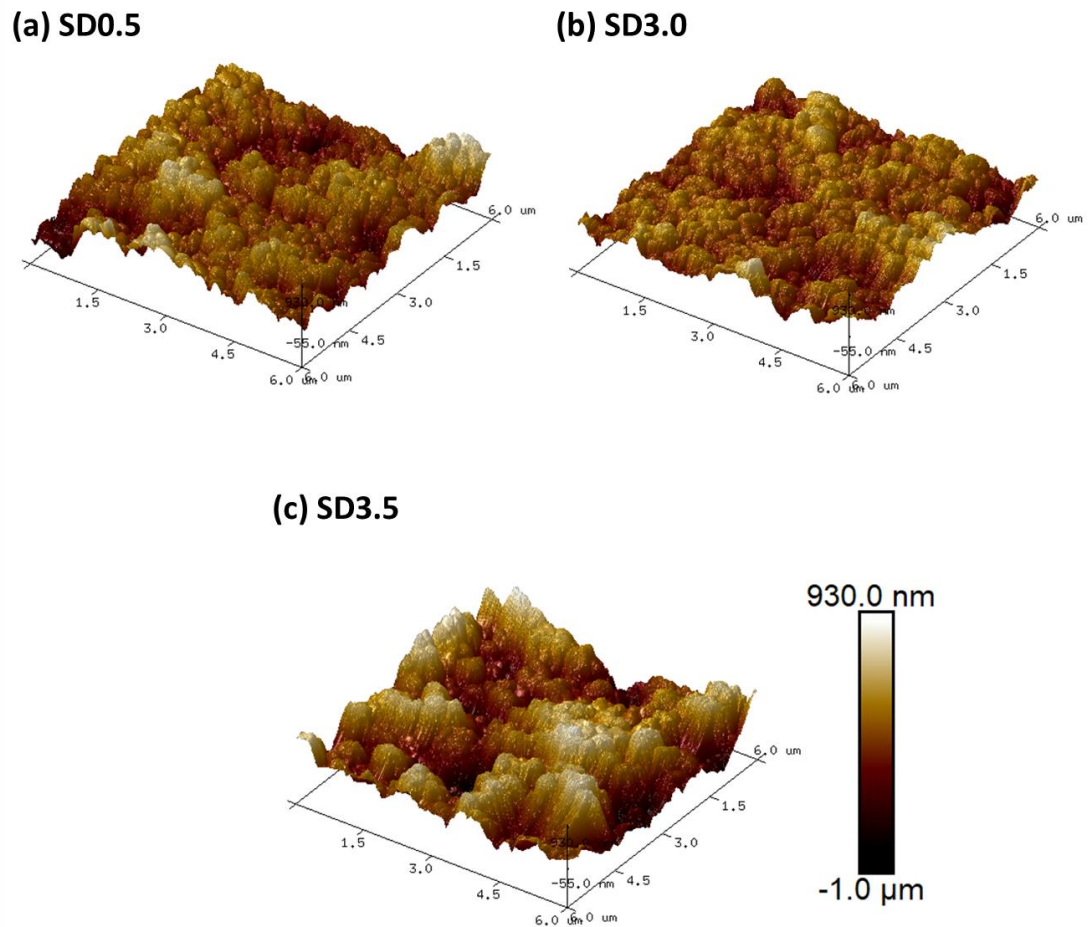


Figure 5.5 - Examples of three-dimensional topographic maps obtained using AFM in Tapping Mode for spray dried titanium dioxide.

For each powder, these two roughness metrics are tabulated in Table 5.3. To test whether or not the roughness metrics were significantly different, a single factor ANOVA (Analysis of Variance) analysis was performed on the Rq and Ra data sets. The ANOVA analysis determined that the null hypothesis was retained indicating that the roughness results for both Rq and Ra metrics were not significantly different. These results therefore demonstrated that all four powders have a similar level of surface roughness.

Table 5.3 - Surface roughness metrics obtained from AFM Tapping Mode analysis for spray dried titanium dioxide.

Powder	Rq (nm)	Ra (nm)
SD0.5	270 ± 20	210 ± 20
SD3.0	210 ± 50	170 ± 40
SD3.5	240 ± 60	190 ± 50

However, it is known that the assessment of roughness using Rq and Ra metrics can have limitations due to the fact that they are influenced by the scanning scale (Mwema et al., 2019). This means that these metrics cannot provide information on the lateral spacing and distribution of surface features. A better description of surface geometries is provided by Power Spectral Density (PSD) functions. PSD functions have the advantage of providing information about the lateral distribution of the surface structures, thereby overcoming the limitations associated with methods such as the root mean square roughness. Furthermore, PSD functions allow roughness data from different lateral distances to be directly compared (Gong et al., 2016). PSD functions express the amplitude of roughness of surfaces as a function of the spatial frequency of surface structures (Bruker, n.d.; Mwema et al., 2019). The spatial frequency is the inverse of the wavelength of the roughness features, i.e, the lateral distances between these features (Bruker, n.d.).

The PSD profiles for spray dried TiO_2 can be found displayed in Figure 5.6. The frequency distribution for a digitized profile of length, L consisting of N points sampled at intervals of d_0 can be approximated by Equation 5.18;

$$PSD(f) = \frac{2d_0}{N} \left| \sum_{n=1}^N e^{\frac{i2\pi}{N}(n-1)(m-1)} z(n) \right|^2 \quad \text{for } f = \frac{m-1}{Nd_0}; \quad 2D \text{ PSD} = \frac{P}{2\pi f \Delta f} \quad (5.18)$$

where frequencies, f range from $1/L$ to $(N/2)/L$. Using this function, the profiles displayed in Figure 5.6 were computed using the Nanoscope Analysis 1.9 software by selecting the 2D Isotropic PSD and then displaying the profile as a 2D Iso plot type.

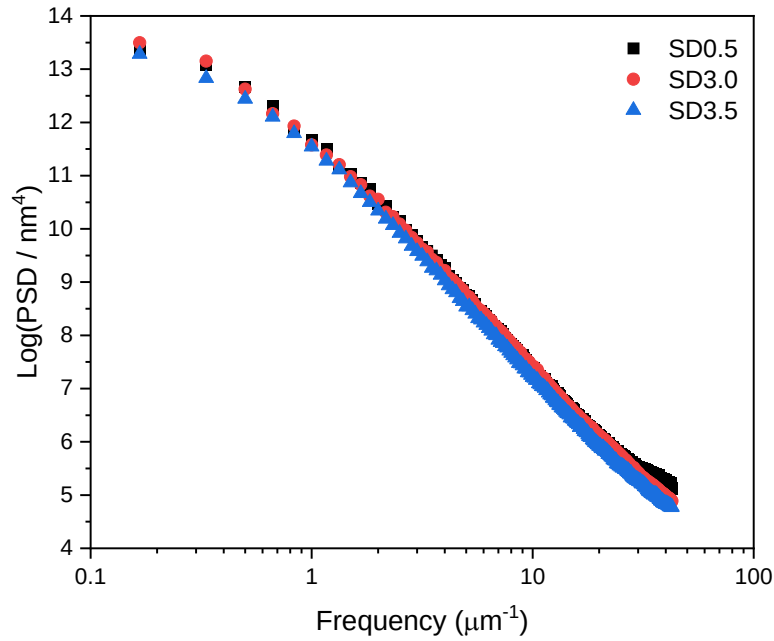


Figure 5.6 - Power Spectral Density profiles obtained for spray dried titanium dioxide.

For all samples, the PSD profiles display a randomly rough surface, i.e. peaks are absent from the profiles which would be present for a surface with periodic structure (Mwema et al., 2019). The spatial frequency on the x-axis represents the surface roughness at various lateral distances between the spatial features (Myers et al., 2021). A higher spatial frequency represents surface features that are closer together, whilst a lower spatial frequency represents surface features which are further apart.

For spray dried titanium dioxide, the PSD profiles displayed in Figure 5.6 can be divided into three distinct length scales. The spatial frequency of $10 - 100 \mu\text{m}^{-1}$ corresponds to inter-spatial distances of $10 - 100 \text{ nm}$. This region of the PSD profile is likely to be influenced by the applied alumina and silica surface coatings, i.e. the surface roughness of the TiO_2 crystallites. Numerous studies have shown that these coatings can have various morphologies (See literature review).

The spatial frequency of $1 - 10 \mu\text{m}^{-1}$ corresponds to the inter-spatial distances of $100 - 1000 \text{ nm}$. Since, the average TiO_2 crystallite has been shown to be approximately $200 - 300 \text{ nm}$, this region of the PSD profile is likely to be affected by the surface roughness created by different TiO_2 crystallite sizes and shapes.

The spatial frequency of $0.1 - 1 \mu\text{m}^{-1}$ corresponds to inter-spatial distances of $1 - 10 \mu\text{m}$. This region of the PSD profile will therefore be influenced by the arrangement of the crystallites.

Furthermore, this length scale is also thought to be most influential to the degree of adhesion/cohesion displayed by the powder as it will influence the contact area during the drop test and the interparticle contact area during powder flow.

Below a spatial frequency of $0.2 \mu\text{m}^{-1}$, the PSD profiles begin to plateau. According to Mwema et al. (2019), the physical meaning of this plateau is that there is no significant variation in the values of the surface roughness at this low frequency, i.e. the largest length scales. Which also means that at the higher frequencies and smaller length scales, the surface roughness varies in a highly correlated manner. For all samples, the PSD profiles were also found to collapse onto a single curve which indicates that the surface roughness of all the spray dried samples are similar.

In this work, it was thought that the surface treatments may have an influence upon surface roughness due to the different morphologies that can form on the TiO_2 crystallites. However, in this work, differences in roughness between samples were not observed. These results may therefore suggest that the surface treatments on the supplied TiO_2 samples contain similar morphologies and that the formed morphologies (and surface roughness) may actually be independent of coating level.

Surface adhesion

AFM in Peak Force Tapping (PFT) mode was employed to study the surface adhesion of spray dried titanium dioxide. Shown in Figure 5.7 are examples of height and adhesion maps obtained for all samples. Visually the 2D height maps show distinct areas which are located at low and high values, which is indicated by darker and lighter areas respectively. Also noticeable in these maps are the TiO_2 crystallites. The adhesion maps demonstrate that SD0.5 is the most adhesive, which is shown by a map which is more lighter in colour, whilst SD3.5 is the least adhesive which is indicated by a map with a more darker colour. SD3.0 appears to display intermediate adhesiveness in comparison to SD0.5 and SD3.5.

The differences observed in the adhesion maps can be attributed to the surface chemistry of the supplied samples. Before drying, the TiO_2 crystallites were coated with hydrous oxides and between the samples, these surface treatments varied. SD0.5 received a surface treatment of 0.5 wt% alumina, SD3.0 was coated with 3.0 wt% alumina, whilst SD3.5 was surface treated with 0.5 wt% silica and then 3.0 wt% alumina. Since the surface treatments varied by the different levels, this could influence the surface coverage of the supplied materials and therefore the adhesion. For example, a 0.5 wt% surface treatment for SD0.5 could be insufficient in coating the surface of TiO_2 , which means the surface of SD0.5 will contain a greater proportion of TiO_2 . Since TiO_2 is more adhesive than alumina (see later), this would result in a more adhesive surface for SD0.5. In contrast, with a surface coating of 0.5 wt% silica and then 3.0 wt% alumina, the

surface coverage of SD3.5 will be greater and less TiO₂ will be present at the surface. Hence, the adhesion map obtained for SD3.5 shows a surface with lower adhesion.

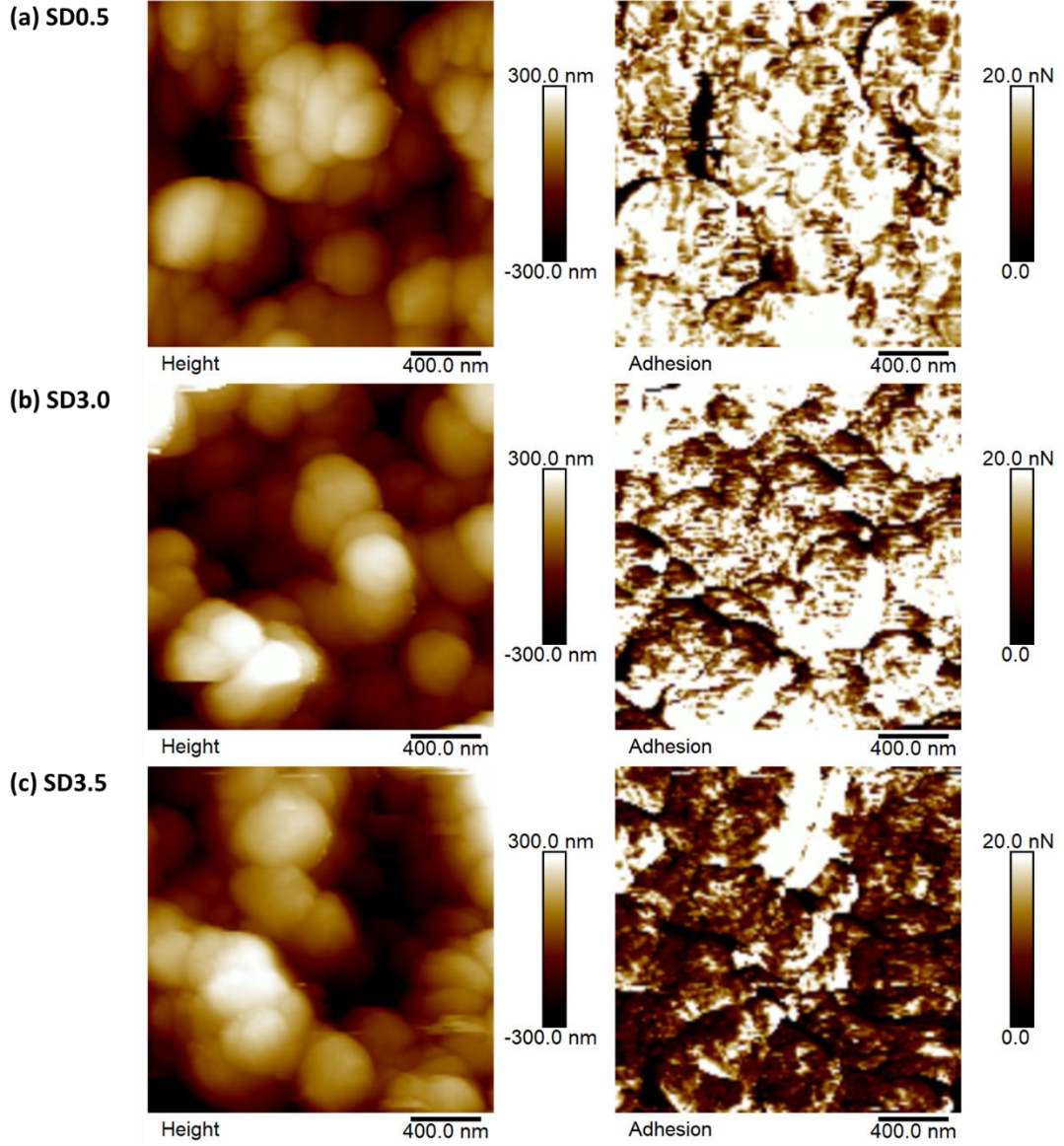


Figure 5.7 - AFM height and adhesion maps for spray dried titanium dioxide.

From each adhesion map, a distribution of adhesion forces were obtained from the mapped area. The distributions were found to follow a log normal distribution of pull-off forces. An example of a typical pull-off force distribution for SD0.5 is displayed in Figure 5.8. In order to obtain the average adhesion value from a distribution, a log normal distribution was therefore applied to the data, Equation 5.19;

$$\frac{dy}{dz} = \frac{1}{\sigma_z \sqrt{2\pi}} \exp \left(-\frac{(z-\bar{z})^2}{2\sigma_z^2} \right) \quad (5.19)$$

where $z = \log x$, $\bar{z}$ is the arithmetic mean of $\log x$ ($\bar{z} = \log \bar{x}$) and σ_z is the standard deviation of $\log x$ (Rhodes, 2008). An example of a fitted log normal distribution is shown in Figure 5.8. From the fitted distributions, mean adhesion values were obtained.

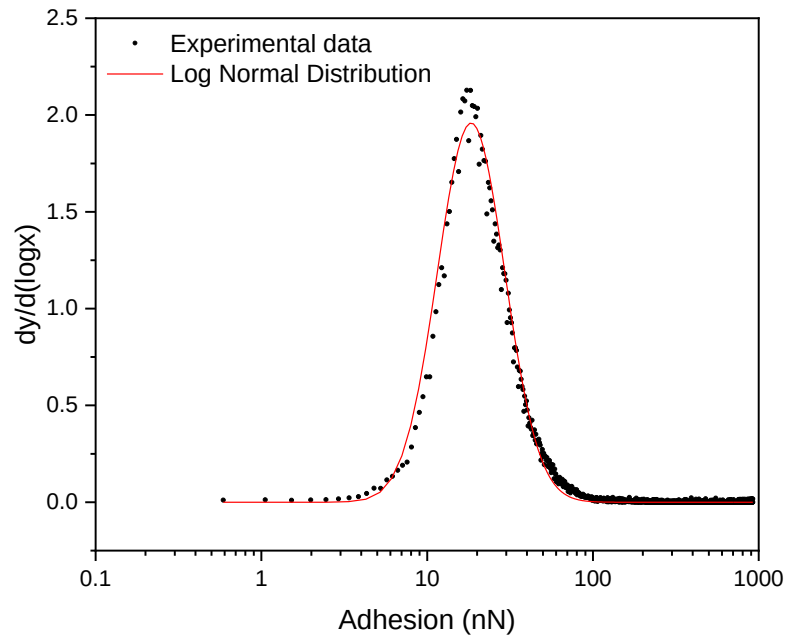


Figure 5.8 – An example of a typical adhesion distribution obtained during AFM peak force tapping experiments over a scan area of $6 \mu\text{m}$.

For each mapped area, the mean adhesion values are reported in the bar chart of Figure 5.9 for each sample. During adhesion mapping, each mapped area was labelled. An example of the notation used is as follows P1A1, where P1 stands for particle 1 and A1 is used to designate the 1st area mapped on particle 1. For each particle, the adhesion values were averaged to give a mean adhesion value for the particle. Then the adhesion values for the particles were further averaged to give a mean adhesion for the sample. The mean adhesion for each sample can be found reported in Table 5.4. Figure 5.9 shows that SD0.5 is the most adhesive. The adhesion values obtained were found to range between 15.7 – 19.6 nN. Figure 5.9 also shows that SD3.5 is the least adhesive, its values were found to range from 5.6 – 11.8 nN. The mean adhesion reported for each sample which is tabulated in Table 5.4 also demonstrates that SD0.5 is the most adhesive, whilst SD3.5 is the least adhesive. Considering SD3.0, its adhesion values ranged 9.3 – 17.5 nN with a sample average of 13 ± 3 nN. In contrast, to SD0.5 and SD3.5, the values obtained for SD3.0 were found to vary much more. This observation is highlighted in the larger range and greater standard deviation. This is also consistent with the adhesion maps obtained for SD3.0 and could indicate towards the more heterogenous nature of the surface for SD3.0. Since, the range of

adhesion values obtained for SD0.5 and SD3.5 are quite narrow and the standard deviations are also smaller, this could also indicate that the surface of SD3.0 and SD3.5 are more homogeneous.

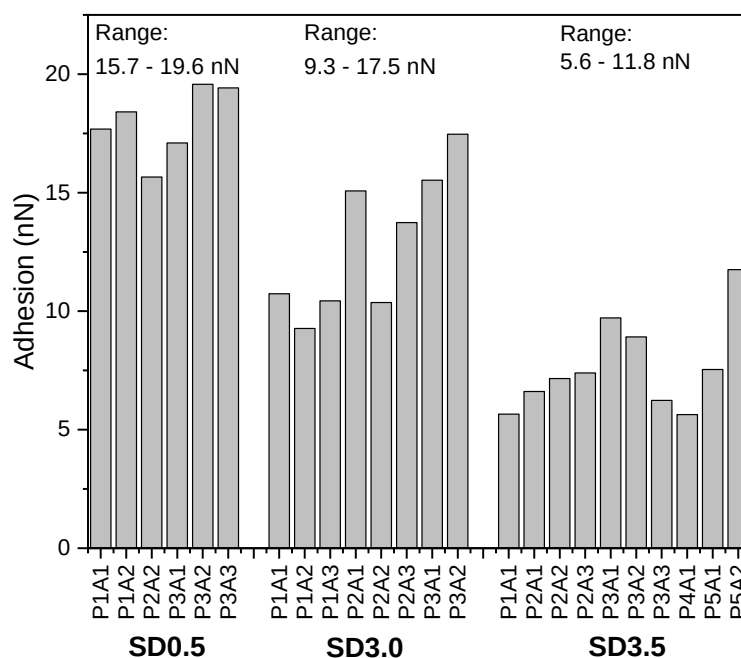


Figure 5.9 - Adhesion values obtained from mapped areas for each sample.

Table 5.4 - AFM adhesion / pull-off force results obtained from 2 μm scans for spray dried titanium dioxide.

<i>Powder</i>	<i>Pull-off force (nN)</i>	<i>Hamaker constant ($\times 10^{-20}$ J)</i>
SD0.5	18 ± 1	6.1 ± 0.7
SD3.0	13 ± 3	3 ± 1
SD3.5	7 ± 1	0.9 ± 0.3

The results obtained from the AFM experiments for SD0.5 and SD3.5 were found to be consistent with the drop test results, where both experiments showed that SD0.5 is the most adhesive powder, whilst SD3.5 is the least adhesive. However, the results from the drop test obtained for SD3.0 did not indicate that the adhesiveness of SD3.0 was significantly different from SD3.5. In contrast, the AFM results suggested that SD3.0 is actually more adhesive than SD3.5. A possible reason for this discrepancy could be due to the much lower resolution of the drop test, where this test is unable to distinguish the difference between particle adhesion for SD3.0 and SD3.5.

Since the magnitude of the Hamaker constant reflects the strength of the van der Waals force interaction between two particles or a particle and a substrate, the Hamaker constants for the

supplied samples were also estimated. These values can be found reported in Table 5.4 and were estimated using Equation 5.20 and Equation 5.21, where Equation 5.20 represents the van der Waal force, F_{vdw} for a sphere of radius, R at a distance of z_0 from a flat surface;

$$F_{vdw} = \frac{A_{12}R}{6z_0^2} \quad (5.20)$$

In Equation 5.21, A_{12} is the Hamaker constant for the sphere-flat surface interaction (Israelachvili, 2011). By using the sphere-flat surface model, A_{12} was estimated for our materials by assuming the flat surface was the sample and the sphere was the silicon probe. In these estimations, F_{vdw} was taken to be the average adhesion force obtained from the PFT analysis, R the radius of the silicon sphere (30.8 nm) and z_0 the standard literature value of 0.165 nm.

Since, A_{12} represents the Hamaker constant for the silicone probe sample surface interaction, the Hamaker constants for the samples, A_{11} were estimated by using Equation 5.21;

$$A_{12} = \sqrt{A_{11}A_{22}} \quad (5.21)$$

where A_{22} is the Hamaker constant of silicon which has been reported to have a value of 15×10^{-20} J (Ku et al., 2023). These estimations showed that the Hamaker constant for SD0.5 is the largest, whilst the Hamaker constant obtained for SD3.5 is the smallest. The relative magnitude of these Hamaker constants are also consistent with the average adhesion values, since the van der Waals force is proportional to the Hamaker constant.

A review of the literature for the Hamaker constants for TiO_2 , Al_2O_3 and SiO_2 revealed that these materials have values of $14.3 - 43.0 \times 10^{-20}$ J, $11.3 - 15.2 \times 10^{-20}$ J, $5.0 - 6.6 \times 10^{-20}$ J respectively (Ackler et al., 1996; Bergström, 1997; Israelachvili, 2011). It is clear from these values that TiO_2 can display a larger Hamaker constant than Al_2O_3 and SiO_2 , and that SiO_2 has the smallest Hamaker constant. Therefore, a surface composed of TiO_2 would be more adhesive in comparison to a surface composed of alumina or silica. Recalling the compositions of the applied surface treatments and therefore the surface compositions of the samples, it is likely that the surface of SD0.5 will contain a higher proportion of TiO_2 with a small amount of Al_2O_3 . In contrast, the surface of SD3.0 will contain a higher proportion of Al_2O_3 with a small amount of TiO_2 exposed, whilst the surface of SD3.5 will be composed mostly of Al_2O_3 with a small amount of exposed SiO_2 . Therefore, the levels of adhesion observed for the supplied samples are consistent with their surface compositions. Noteworthy, the calculated Hamaker constants obtained for the supplied materials were lower in comparison to the literature Hamaker constants for TiO_2 , Al_2O_3 and SiO_2 . However, some variability would be expected, i.e. a surface composed of TiO_2 and Al_2O_3 would be expected to have a Hamaker constant between TiO_2 and Al_2O_3 , but this trend is not observed in the estimated values. Therefore, this discrepancy can probably be attributed to the

nanoscale roughness which influences the contact area between the AFM probe and the samples surface resulting in a slightly lower adhesion force being measured and hence a lower Hamaker constant being estimated.

Based upon the results observed for the spray dried samples, the adhesive behaviour of SFD3.5 could be postulated. It is very likely that the surface roughness of spin flash dried SFD3.5 will be similar to the spray dried samples, which also means that the adhesive behaviour of SFD3.5 would be dictated by its surface chemistry. To recap, SFD3.5 was surface treated with 0.5 wt% zirconia and 3.0 wt% alumina. The Hamaker constant of zirconia is 20×10^{-20} J. Therefore, SFD3.5 is likely to have a similar adhesiveness to SD3.0, but its adhesion will be significantly lower in comparison to SD0.5. This hypothesis would also be consistent with the results obtained during the drop test experiments.

5.4 Conclusions

During bulk powder handling, the adhesion and cohesion of fine particles can cause undesirable effects such as unpredictable or unreliable flow and blockages. Therefore, during this chapter, the adhesion and cohesion of spray dried and spin flash dried titanium dioxide featuring different surface treatments was investigated. Two techniques were employed. The drop test which was utilised to investigate the overall adhesive behaviour of each sample, whilst AFM was used to understand the contributions of the surface roughness and the surface chemistry to the overall sample adhesion.

The drop test showed that SD0.5 was the most adhesive powder, whilst SD3.0, SFD3.5 and SD3.5 were shown to be the least adhesive. The drop test was unable to distinguish the adhesiveness between SD3.0, SD3.5 and SFD3.5. AFM TM experiments showed that the surface roughness of the spray dried samples were similar, whilst the AFM PFT experiments confirmed that the relative adhesiveness of each sample was dictated by the surface chemistry and the applied surface treatments. Since the level of adhesion observed is due to the van der Waal forces, it can also be concluded that the adhesion will correlate with cohesion, i.e. if one sample is more adhesive, then it will also be more cohesive.

Overall, for spray dried and spin flash dried surface treated titanium dioxide, this study demonstrates that when the surface of the titanium dioxide is coated heavily with silica and alumina surface treatments, then a powder is produced which is much less cohesive. Thus, for better processing and better powder handling, silica and alumina surface treatments will be beneficial.

Chapter 6 – Structure, strength and breakage

6.1 Introduction

During handling and conveying, particulate materials in the form of agglomerates and granules can be subjected to breakage processes. It is also known that breakage leads to changes in bulk handling behaviour since it leads to a change in the properties of the particulate material such as its size distribution and bulk density (Bemrose and Bridgwater, 1987). It has been established that the resistance to breakage correlates with the bulk strength of the agglomerates (Adams and McKeown, 1996). Therefore granule strength plays an important role in the bulk handling of granular materials. In this study, it has thus been important to consider how breakage may influence the bulk handling behaviour of spray dried and spin flash dried titanium dioxide. In Chapter 4, particle breakage via frictional and shear forces was investigated through the use of the Schulze shear cell and it was found that no significant breakage had occurred under the conditions investigated. In this chapter, particle breakage is investigated further.

Like most particulate solids, granular matter is rarely a monodispersed system and a range of sizes will be present. The individual granules are assemblies of smaller particles held together by adhesive forces (Bika et al., 2001; Reynolds et al., 2005). These adhesive bonds can be solid bridges, capillary, or van der Waal interactions (Reynolds et al., 2005). In terms of spray dried powders, the granules are formed from slurries which are atomised into droplets, which are then dried into granules. To adhere the primary particles together, a binder is usually formulated into the slurry and during the droplet drying process, the binder will form solid bridges, the adhesive bonds which bind the primary particles together inside the granule. Since the solid bridges are much weaker than the primary particles, during a stressing event, the solid bridges will be ruptured leading to fracture and breakage of the granule (Reynolds et al., 2005).

The bulk strength of granular solids are size, composition and structure sensitive. Particle size is probably the most important factor. This is because larger particles are known to be weaker than smaller particles, which is due to the fact that smaller particles contain smaller flaws and micro-cracks and there is a change from brittle to plastic behaviour (Bemrose and Bridgwater, 1987). Composition is also influential. As stated, for spray dried granules, the composition of the granules will largely include the primary particles and some form of a binding substance. A higher binder content will provide stronger adhesive bonds between the primary particles thereby increasing granule strength. When solid bridges exist, these types of bonds will also be the primary strength determining bonds within the granule (Salman et al., 2007). Within the structure of a granule, a void space will also exist. Generally, a greater void space will lead to a weaker structure since there are fewer primary particles and interparticle bonds.

Micromechanical models can be used to describe the composition-structure-strength relationship. Perhaps the best known expression which relates the composition and structure to the tensile strength of the granule was given by Rumpf (1962). Rumpf simply describes granule tensile strength as the tensile force at failure divided by the cross-section of the agglomerate and is suggested to be the summation of all the interparticle bond forces across the fracture surface (Salman et al., 2007). Hence, greater numbers of stronger bonds and a low porosity (void space) will afford stronger granules.

In the literature, granule strength is not well defined. However, it is usually interpreted as the resistance to permanent deformation and fracture during a stressing event (Bika et al., 2001; Reynolds et al., 2005). Furthermore, it is the conditions which are applied to the material during a stressing event which will define the strength of a granular material. Granule tensile strength is usually determined by compressing a single granule between two platens. However, during bulk handling, particles are more likely to suffer breakage by impact rather than by compression, for example during pneumatic conveying at the bend of a pipe. It could be argued that breakage by compression and impact are very different processes. However, it has been suggested that these processes are actually quite similar. This is because in both processes, a particle will experience some form of compression and tensile stress will be induced (Lister, 2016). Previous studies have also shown that slow compression and low-velocity impacts induce similar stress fields. For example, see Arbiter et al. (1969) who investigated the fracture of sand-cement spheres during quasi-static compression and free-fall impact experiments or Shipway and Hutchings (1993) who investigated the attrition of brittle glass spheres.

Moreover, many studies have also indicated that composition-structure-impact breakage relationships share many similarities with composition-structure-strength correlations. For example, Subero et al. (1999; 2000) demonstrated that a higher binder content was found to produce stronger agglomerates which showed greater resistance to breakage. A higher binder content was thought to produce stronger bonds between the primary particles and they conversed that stronger bonds were able to transmit higher loads without failing. Furthermore, several investigators have studied the influence of porosity on breakage. These studies demonstrated that at the same impact velocity, breakage extents became more severe with increasing void fractions (Subero et al., 2000; Mishra and Thornton, 2001; Samimi et al., 2003). These similarities therefore suggest that granule tensile strength measurements are actually a good indicator as to whether a granular material is likely to be susceptible to breakage by impact.

Since strength and breakage are structure sensitive properties, the structure of the supplied materials have been studied. Initially, structural analysis has been qualitatively undertaken using microtome sectioning with SEM and SEM-FIB. Since, spray dried granules are known to exhibit

a range of structures from solid throughout to hollow constructions (Walton, 2000), these examinations have enabled visual assessment and identification of the types of bonds holding the primary particles together.

Later, Low Field NMR supported by tapped density measurements and image analysis of SEM-FIB images were employed to quantitatively determine the porosity of the supplied materials. Porosity measurements were undertaken using LF-NMR as this method uses an organic solvent to saturate the granule pore space under low pressure conditions allowing the porosity of fragile granulates to be measured. In contrast, mercury intrusion porosimetry utilises high pressures which increase incrementally (Sørland et al., 2007). These pressures can cause breakage of fragile granules which can therefore result in poor porosity results. A disadvantage of LF-NMR is the fact that it can be difficult to determine the intergranular and intragranular contributions to the porosity, and this is where data from FIB-SEM and tapped density measurements can help to provide supportive data. FIB-SEM analysis produced cross-sectioned images of granules. In doing so, the internal structures of the granules could be analysed using image analysis to acquire porosity data. Comparing this data against the LF-NMR data has helped to determine the contributions of the inter and intra granular porosity contributions. However, a limitation of porosity data obtained from FIB-SEM is due to statistical reliability, since the data is based upon single granules which are chosen at random. In contrast, the LF-NMR is a bulk analysis technique and therefore provides much better statistical reliability. Tapped density measurements have allowed determination of the total porosity of the sample and these results provided a useful comparison against the total porosities obtained from LF-NMR data.

Typically granule strength is determined using unconfined uniaxial compression which subjects a single granule to compression between two platens (Lister, 2016). However, this method can be extremely time consuming as typically, 100 - 200 agglomerates have to be tested. Furthermore, these experiments are known to result in a wide distribution of values (Adams and McKeown, 1996). Therefore in this work, the simpler method of confined uniaxial compression of agglomerate beds was employed. This method involved confining a bed of agglomerates in a cylindrical cell and measuring the force applied to a flat piston as a function of displacement (Adams and McKeown, 1996). The first inflection point in the obtained compaction curve was then assumed to be the point at which granules are crushed into their primary particles, thereby providing a measure for the average granule strength. Theoretical models (Adams and Kawakita) were also employed to obtain a measure for the average granule strength. Since previous works have shown that granule strength measured by confined uniaxial compression tests are in good agreement with the single particle strength determined from single particle compression tests (Adams and McKeown, 1996; Marigo et al., 2014), this method was therefore deemed appropriate for determining the strength of spray dried and spin flash dried titanium dioxide granules.

Review of fracture mechanics theory

As stated, granular powders are rarely monodispersed systems and a range of sizes will exist. Moreover, it is well known that the breakage strength of particles increases markedly as the diameter decreases. This is due to the fact that flaw sizes and microcracks become smaller at smaller particle sizes (Bemrose and Bridgwater, 1987; Tavares, 2007). The relationship between particle strength and flaw size can be described by Griffith's criterion (Lister, 2016), which relates the critical stress, σ_T required to propagate a crack of length, L (Equation 6.1);

$$\sigma_T \propto \left(\frac{2\gamma E}{L} \right)^{1/2} \quad (6.1)$$

where γ is the surface energy of the material and E is the young's modulus. When the strain energy exceeds the surface energy, crack propagation will occur. Griffith's criterion demonstrates that granule strength will be higher when the flaw size is smaller.

During handling and transport, granules will experience impact against pipes walls. When a particle undergoes impact, the contact zone will be compressed and pressure waves will be transmitted through the particle causing a tensile stress to be induced, consequently leading to failure and breakage (Lister, 2016). Similarly, when a particle undergoes compression between two platens, tensile stress is induced and failure of the particle occurs. This process can be described by Equation 6.2, which relates the tensile stress which is induced along a plane parallel to the compression points to the applied compression force, F_c and the cross-sectional area under tension, πd^2 ;

$$\sigma_T = \frac{4F_c}{\pi d^2} \quad (6.2)$$

Equation 6.2 demonstrates the fact that particle tensile strength scales with particle size and that a compression force of similar magnitude would be required to break a smaller particle and a larger particle.

When a particle is impacted against a hard flat surface such as a pipe wall, the particle will fracture if the pressure generated on impact exceeds the tensile strength of the particle. At a low impact velocity, failure of the particle may occur via a central crack (Lister, 2016). Whilst at higher impact velocities, a conical zone of fines is found to form due to deformation of the contact point, with radial cracks extending from this point. Usually at a higher impact velocity, the breakage extent of a particle, which can be interpreted as the mass of material lost from the original particle mass is greater. This relationship between breakage extent, R^* and impact velocity, v is demonstrated in Equation 6.3 (Ghadiri and Zhang, 2002; Zhang and Ghadiri, 2002);

$$R^* = \alpha v^2 \frac{\rho d H}{K_c^2} \quad (6.3)$$

where α is a proportionality factor and ρ , d , H , K_c is the density, size, hardness and fracture toughness of the particle. The model presented in Equation 6.3 also shows two other important relationships. The 1st is the relationship between breakage extent and particle size, which is consistent with the fact that a larger particle is weaker than a smaller particle and therefore its extent of breakage would be expected to be greater. The 2nd relationship is between the breakage extent and the mechanical properties of the particle, where R^* is a strong function of K_c , since this parameter is to the power of 2. Furthermore, it is known that the fracture toughness is proportional to the granule strength (Equation 6.4);

$$K_c \propto \sigma_T(\pi L)^{1/2} \quad (6.4)$$

which demonstrates the fact that particles which have a higher toughness and greater strength will be less susceptible to breakage. Moreover, these models also demonstrate the fact that granule tensile strength measurements are a good indicator as to whether a granular material is likely to be susceptible to breakage.

6.2 Materials and methods

6.2.1 Microtome sectioning and scanning electron microscopy

In order to image the internal structure of spray dried and spin flash dried titanium dioxide granules, powder samples were embedded in an epoxy resin (Epofix cold mounting resin, Struers Ltd, UK) in Eppendorf tubes and allowed to cure over a period of 24 hours. Once cured, the resin embed samples were then microtome sectioned using a diamond knife on a Reichert-Jung Ultracut E microtome. The cross-sectional area of the sectioned samples were then smoothed. The resin embedded samples were then attached to aluminium stubs and coated with 10 nm of iridium for SEM imaging.

Prepared microtome samples were then imaged using scanning electron microscopy. During this work, an Hitachi SU8230 Cold Field Emission (CFE) Scanning Electron Microscope (Oxford Instruments) was employed.

6.2.2 Focussed ion beam scanning electron microscopy

The structure of spray dried and spin flash dried granules were also investigated using a FEI Helios G4 CX DualBeam, High resolution monochromated FEGSEM with precise Focused Ion Beam (FIB). Prior to analysis, samples were adhered to carbon stickers and coated with approximately 20 nm of iridium. During the analysis and before milling, a platinum protection bar with an area of $30 \times 2 \mu\text{m}$ and a thickness of $1 \mu\text{m}$ was applied to aid the production of a smooth cross section and to prevent curtaining.

6.2.3 Low-field NMR

Fluid filled porosity was measured using a Maran Ultra NMR Analyser (Oxford instruments), a low-field benchtop NMR instrument. Samples were analysed using a Carr-Purcell-Meiboom Gill (CPMG) sequence in order to acquire the transverse (T_2) relaxation time. The T_2 relaxation time reveals important information about the structure of porous materials and it can be used to obtain the porosity.

Low-field NMR is based upon differences between the relaxation times of hydrogen containing molecules when confined, in comparison to those in the bulk liquid (Habina et al., 2017). Values of relaxation times of molecules located close to a pore surface are shorter due to the intermolecular interactions with the solid surface. The measured T_2 relaxation time can be expressed by the following formula, Equation 6.5;

$$\frac{1}{T_2} = \frac{1}{T_{2,B}} + \frac{1}{T_{2,S}} + \frac{1}{T_{2,D}} = \frac{1}{T_{2,B}} + \frac{\rho S}{V} + \frac{1}{T_{2,D}} \quad (6.5)$$

where $T_{2,B}$ is the relaxation time for the bulk fluid, $T_{2,S}$ is the surface relaxation time and $T_{2,D}$ is the diffusion relaxation time (Li et al., 2014).

When a porous media is saturated with a hydrogen rich fluid, intermolecular solid-fluid forces dominates the relaxation mechanism and therefore $T_{2,S}$ is the main component. Therefore, Equation 6.5 can be simplified to Equation 6.6 (Li et al., 2014);

$$\frac{1}{T_2} \approx \rho \frac{S}{V} \quad (6.6)$$

where ρ is a proportionality constant and S/V is the surface area to volume ratio which for cylindrical pores is equal to $3/r$, where r is the pore size (Li et al., 2014). Equation 6.6 can also be rearranged to give Equation 6.7;

$$T_2 = \frac{1}{\rho} \frac{V}{S} = \frac{1}{\rho} \frac{r}{3} = Cr \quad (6.7)$$

Equation 6.7 relates T_2 to r via the constant, C . Therefore, C allows the conversion of T_2 to the pore radius (or diameter). During our analysis, a comparison of mercury intrusion porosimetry results with T_2 distributions was utilized for the determination of C , which was found to have a value of 89.1 ms/ μm . Only granules which displayed robustness to the high pressure was used during mercury porosimetry analysis.

For NMR analysis, the TiO_2 samples were prepared by dispersing approximately 10 g of sample in 50 ml of isopropyl alcohol (IPA). The dispersed samples were then placed in a desiccator under vacuum for 4 hours to degas the sample and saturate the pore space. The removal of trapped air allowed the IPA to enter the pores within the granules. IPA was used as a saturant as it has a low

surface tension. On removal of the vacuum, the mixture was allowed to settle, and excess IPA was removed from the sample. During the analysis, each sample was scanned a total of 100 times and before analysing any samples, a bulk sample of IPA was run as a blank.

6.2.4 Confined uniaxial compression

Confined uniaxial compression measurements were performed using a mechanical testing machine (Model 5566, Instron Corp., USA). Powder samples were loaded into a stainless steel cylinder shaped sample die with a height and internal diameter of 20 mm. During loading, the sample and die was repeatedly tapped and filled with powder until the sample cell was completely filled and the sample volume did not decrease with any further tapping. A close-fitting stainless steel piston attached to a 10 kN load cell was used to compress the powder. During compression, the force applied to the powder sample was recorded as a function of the extension of the piston.

6.3 Results and discussion

6.3.1 Granule structure

Spray dried granules are known to exhibit a range of morphologies and structures, from spherical to buckled morphologies which may have solid throughout or hollow constructions (Walton, 2000), therefore in this work the internal structures of the supplied powders have been investigated by using microtome sectioning with SEM and Focussed-Ion Beam (FIB) SEM.

Displayed in Figure 6.1 are SEM images of granules which have been embedded in resin and then microtome sectioned. These images clearly show cross sectional areas and the internal constructions of the supplied granules. The microtome images evidently display granules with solid throughout constructions. Also displayed in Figure 6.2 are examples of images obtained during FIB-SEM analysis. The images located on the left display images of granules which were randomly selected for FIB-SEM analysis, whilst the images on the right display images of the same granules which were subjected to the FIB sectioning. Consistent with microtome sectioning results, these images also display granules which exhibit solid throughout constructions. Our analysis was also found to consistent with the work of Li (2019) who prepared spray dried TiO_2 with and without alumina coating from flocculated and highly dispersed feed slurries. In the work of Li (2019), SEM analysis of microtome sectioned samples and FIB-SEM analysis were also used and demonstrated that the spherical and buckled spray dried granules displayed solid throughout structures.

To acquire more information on the internal structures for the supplied granules, SEM images were undertaken at a much higher magnification (200,000x). These images are displayed in Figure 6.3 and clearly show the internal structure of the granules, which consist of assemblies of TiO_2

crystallites held together by some sort of fibrous material. This fibrous material is most evident in Figure 6.3b, 6.3c and 6.3d and is less evident in Figure 6.3a. The nature of this material is most likely to be the alumina, silica and zirconia surface treatments. For SD0.5 (Figure 6.3a) the amount of surface treatments added is much lower at around 0.5 wt%, in comparison to SD3.0, SD3.5 and SFD3.5 where the quantity of surface treatment is at 3.0 / 3.5 wt%. Within the internal structure, the surface treatments also form solid bridges between the crystallites. Examples of solid bridges can be found in a2, b2, c2 and d2. Before drying, with some bonding to the TiO_2 surface, it is highly likely that the surface treatments are present as an inorganic polymeric gel within the titanium dioxide slurry and when atomised into droplets, the solid bridges are formed between the TiO_2 crystallites when the droplets are dried into granules. Therefore, within the titanium dioxide granules, the surface treatments appear to be acting as an adhesive or binder holding the TiO_2 crystallites together. This idea that the alumina acts as an adhesive has also been noted by Zhang et al. (2009), who precipitated alumina on the surface of TiO_2 and reported that the alumina coatings adhered the TiO_2 particles together. The idea that the surface treatments are acting as solid bridges is also not unreasonable to suggest. According to Bika et al. (2005), in granulation, the drying of binders in the form of solutions leads to the formation of solid bridges and depending on the type of binder employed, the solidification process can result in bridges with complex morphologies and microstructures.

Also noticeable within the internal structure of the granules are TiO_2 aggregates, for example see a1 in Figure 6.3a. It is apparent that these aggregates are made from more than one TiO_2 crystallite, but boundaries between the individual crystallites cannot be distinguished. These aggregates are therefore likely to be formed during the chlorination process when the TiO_2 crystallites are formed.

Other observations of the internal structures also show that the granules are porous with interconnecting pore networks. For a given formulation, it is not expected that the porosity will be granule size dependent. This is because during droplet drying, moisture is evaporated from the droplet which leads to aggregation of the TiO_2 particles. As the drying proceeds, the particles inside the droplet reach a maximum packing fraction. Therefore, regardless of droplet size, the ratio of the solid to the liquid phase is the same, which means that granules of different sizes are formed with the same void space.

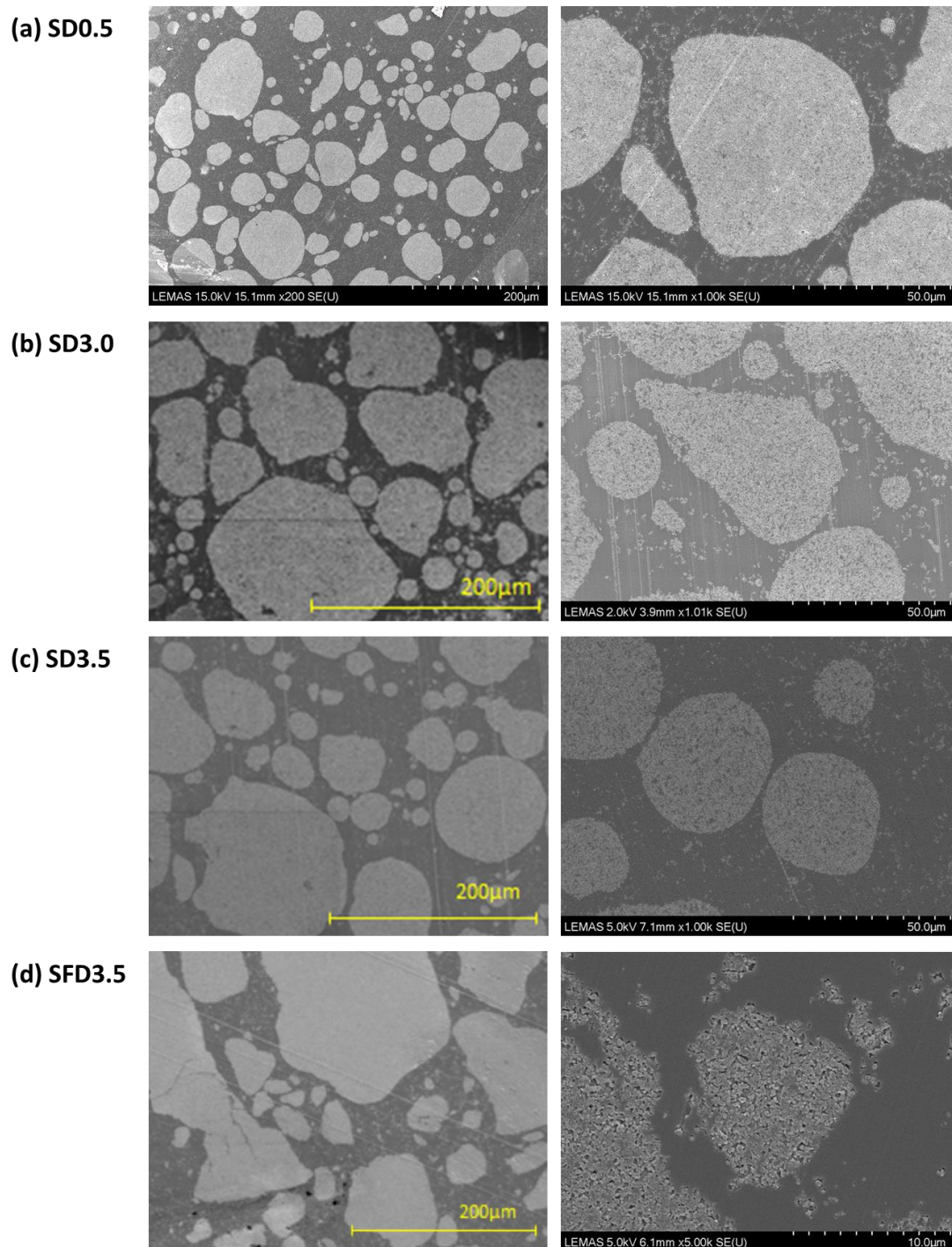
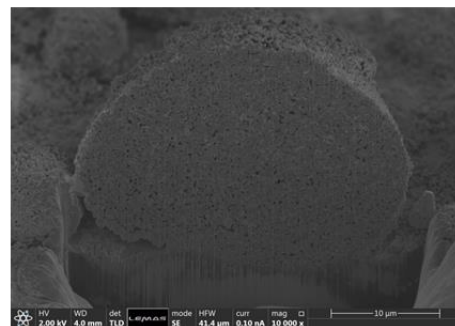
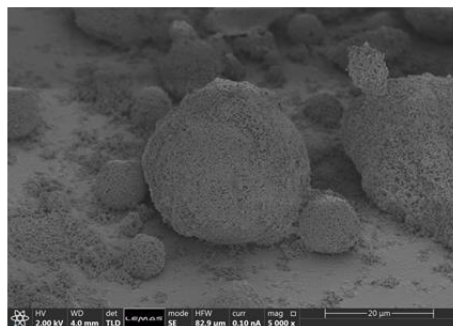
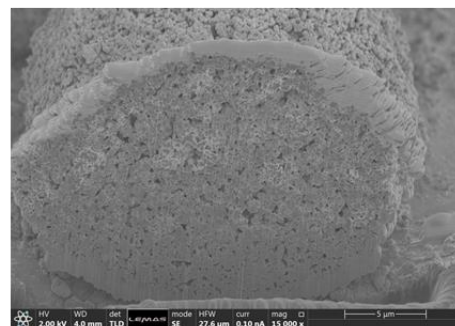
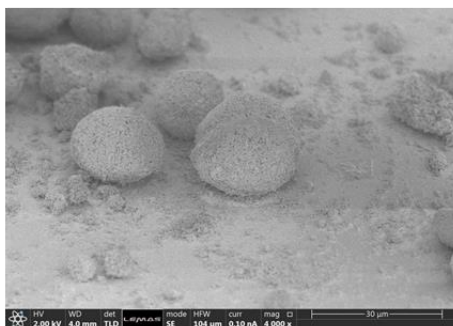


Figure 6.1 - Microtome sectioning and SEM analysis of the internal granule structures for spray dried and spin flash dried titanium dioxide.

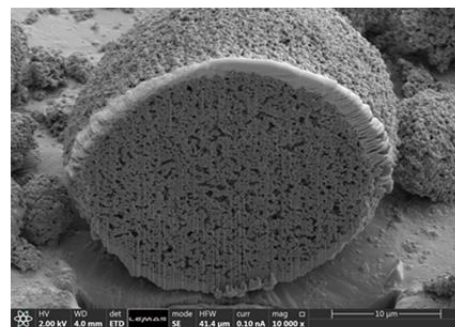
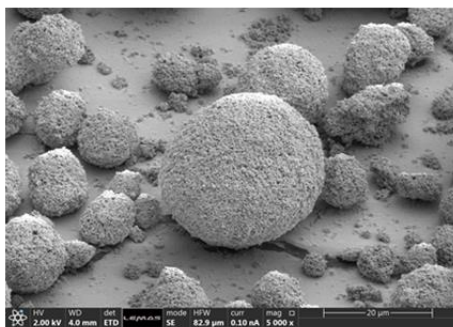
(a) SD0.5



(b) SD3.0



(c) SD3.5



(d) SFD3.5

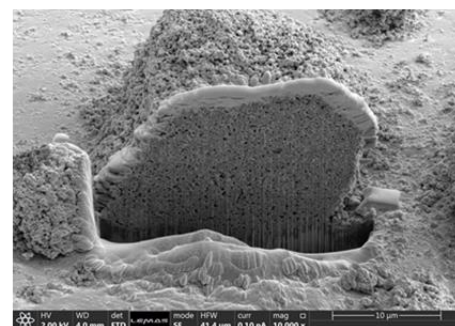
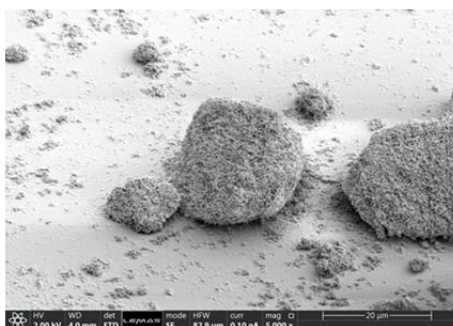


Figure 6.2 - Examples of images obtained during FIB-SEM analysis. Images on the left display granules which were selected for FIB-SEM analysis, whilst images on the right show typical images of cross-sectioned samples.

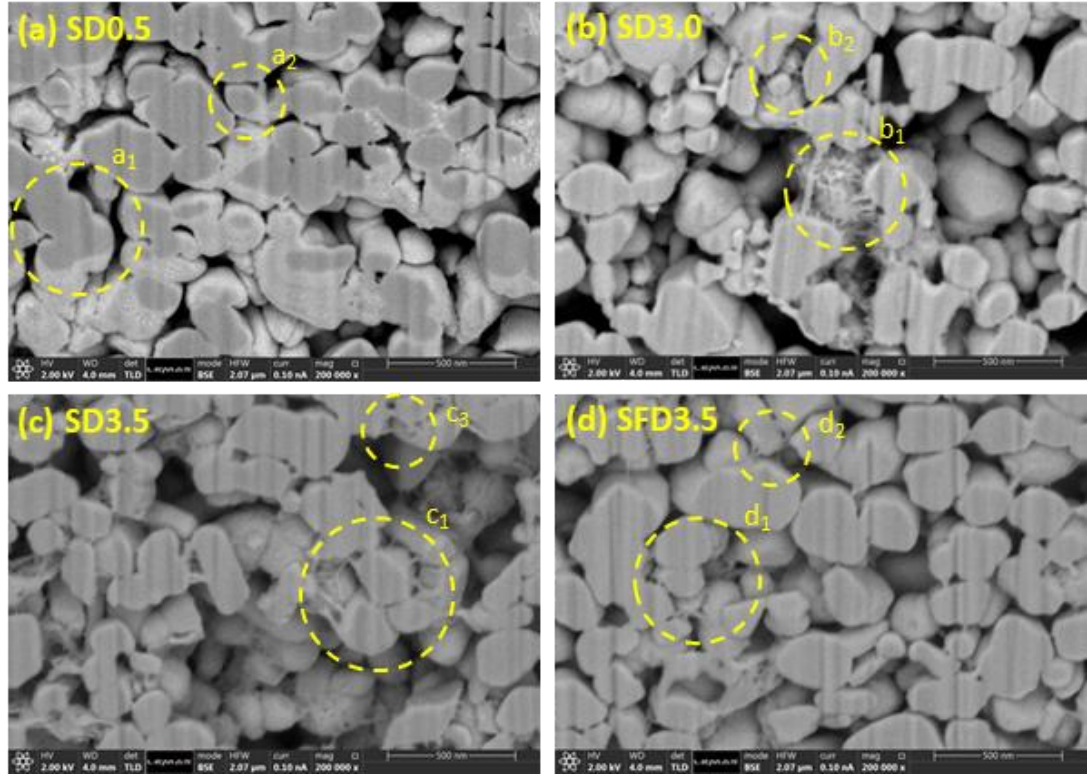


Figure 6.3 - Images of the internal structures of spray dried and spin flash dried titanium dioxide granules taken at 200,000x magnification.

6.3.2 Granule porosity

Microscopy analysis identified that the spray dried and spin flash dried granules were porous in nature and since the strength and breakage behaviour of granules and agglomerates are highly influenced by their porosity, the porosity of the supplied materials has therefore been assessed using three complimentary techniques; dry tapped porosity, low-field NMR and FIB-SEM.

Determined from solid and tapped density measurements which are reported in Chapter 4, dry tapped porosity provides a useful measure for assessment of the samples total porosity and also serves to provide a useful comparison against the total porosity obtained from LF-NMR data. The dry tapped porosity includes both the pore space between the granules (inter-granule porosity) and the pore space within the granules (intra-granule porosity). The dry tapped porosity, P_{tap} is defined in Equation 6.8;

$$P_{tap} = \frac{\rho_s - \rho_t}{\rho_s} \times 100\% \quad (6.8)$$

where ρ_s and ρ_t are the solid and dry-tapped densities respectively.

To further complement and support the porosity data obtained from Low-Field NMR, image analysis of FIB-SEM micrographs were undertaken, where the intra-granule porosity was determined from the pore area, A_p divided by the total image area, A_{total} (Equation 6.9);

$$P_{FIB} = \frac{A_p}{A_{total}} \times 100\% \quad (6.9)$$

For porosity determined by LF-NMR, the total sample porosity, P_T was obtained from the volume of IPA determined from the LF-NMR signal and was calculated using Equation 6.10;

$$P_T = \frac{V_{NMR}}{V_S + V_{NMR}} \times 100\% \quad (6.10)$$

where V_{NMR} is the volume of IPA determined by LF-NMR and V_S is the samples solid volume determined from the mass of sample used and its solid density.

In order to obtain information on inter and intra granular porosities, it was important to identify the inter and intra granule pore regions of the LF-NMR pore size distributions. The obtained pore size distributions from LF-NMR data are displayed in Figure 6.4. In Figure 6.4, two types of LF-NMR distributions are displayed. The first LF-NMR distribution labelled as LF-NMR featuring a black dashed line contains both the inter and intra granular pore sizes, whilst the distribution with a solid black line labelled as LF-NMR (Intra only) contains only the intra-granule pore size distribution. This pore size distribution has then been normalised so it's area is equal to 100%. It must be stated here that the assignment of inter and intra granular porosities to different areas of the LF-NMR pore distributions shown in Figure 6.4 is an assumption. This is because it is quite possible that the pore size distribution areas may have combinations of intra and inter granular pore diameters. However, the pore size distributions obtained from image analysis of FIB-SEM images are also displayed in Figure 6.4 (blue dash dot line) and are compared against LF-NMR data to demonstrate that in our case, this assumption is valid!

By determining the fractional contributions of the inter and intra-pore volumes to the LF-NMR distributions, the intra-granule porosities were then calculated using Equation 6.11;

$$P_{intra} = \frac{V_{intra}}{V_S + V_{intra}} \times 100\% \quad (6.11)$$

where V_{intra} is the intra-granule pore volume.

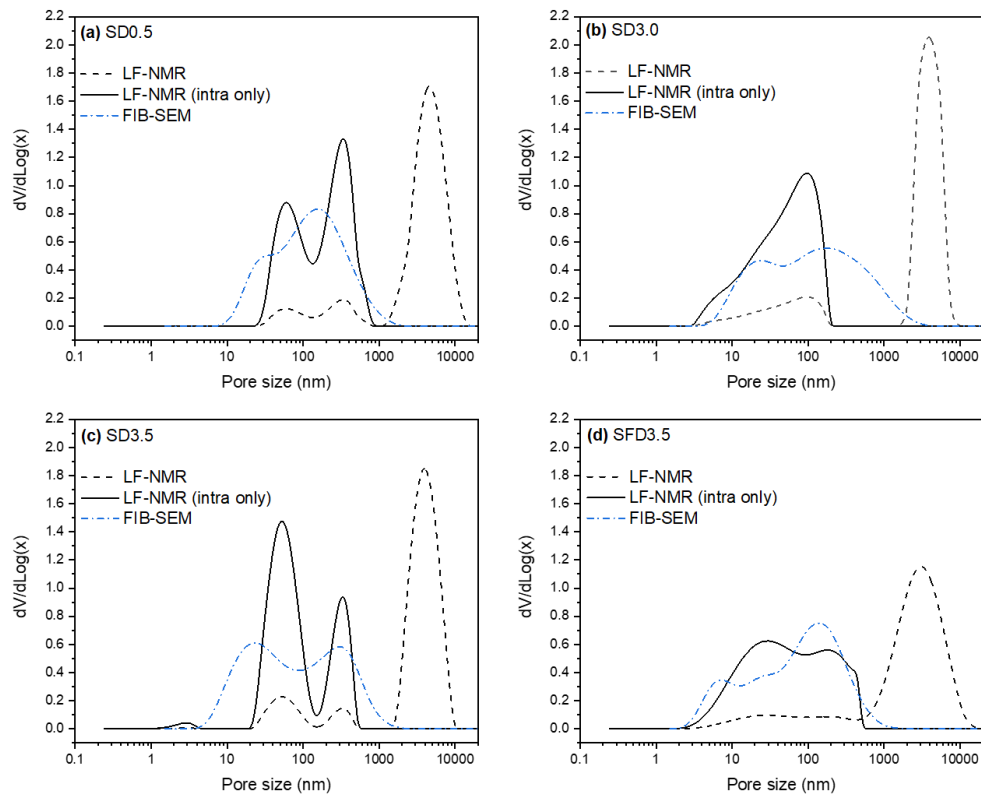


Figure 6.4 - Low-field NMR pore size distributions obtained for spray dried and spin flash dried titanium dioxide. Note: the plot is divided into two main areas (1) inter-granule pores and (2) intra-granule pores.

The porosity data obtained from the three techniques; dry tapped porosity, FIB-SEM and LF-NMR can be found tabulated in Table 6.1. Comparison of tapped porosities to total porosities for SD3.5 and SFD3.5, shows that the results obtained from both tests agree relatively well. In contrast, the tapped porosities obtained for SD0.5 and SD3.0 are higher than their total porosities. This difference can be explained by the fact that SD0.5 and SD3.0 are the most cohesive powders and the fact that the application of a vacuum to draw the IPA into pore spaces is able to overcome these cohesive forces, compacting the solid granules into a smaller volume. For tapped density tests, it is known that for cohesive powders, sometimes the tapping force can be insufficient to overcome the cohesive interparticle forces and this can prevent the powder bed from being consolidated when tapped (Freeman et al., 2017), which explains why the porosity is higher for the tapped porosities.

The intra-granular porosities obtained from FIB-SEM and LF-NMR were found to compare relatively well, proving that the two techniques are complimentary. However, it must be recalled that the FIB-SEM porosity is based upon the analysis of a single granule, whilst the LF-NMR porosity is acquired from bulk sample analysis. This fact is also reflected in their respective data sets, where the LF-NMR porosities show better reproducibility's in comparison to FIB-SEM

porosities. Therefore in this work, the LF-NMR data is referred to as the main porosity dataset, with the FIB-SEM porosity data merely providing support. The intra-granular porosities determined for SD0.5, SD3.0 and SD3.5 were all found to display a porosity of 24.0 – 24.7% and SD3.5 was found to be the most porous with a porosity of 29.3%. Noteworthy, the porosity of the spin flash dried material was not found to be significantly different in comparison to the spray dried materials.

Table 6.1 - Dry tapped, FIB-SEM and Low-field NMR porosities determined for spray dried and spin flash dried titanium dioxide.

<i>Powder</i>	<i>Dry tapped</i>	<i>FIB-SEM</i>	<i>Low-field NMR</i>	
	P_{tap} (%)	P_{FIB} (%)	P_T (%)	P_{Intra} (%)
SD0.5	74 ± 1	23 ± 5	69.4 ± 0.3	24.3 ± 0.7
SD3.0	71 ± 1	31 ± 7	65.7 ± 0.3	24.7 ± 0.7
SD3.5	72 ± 2	28 ± 6	72.8 ± 0.3	29.3 ± 0.8
SFD3.5	65 ± 1	20 ± 5	63.4 ± 0.4	24.0 ± 0.7

6.3.3 Confined uniaxial compression

To determine granule strength, the supplied materials were subjected to confined uniaxial compression tests by compressing a cylindrical powder bed with a piston. A typical load versus extension curve obtained during these experiments is shown in Figure 6.5a. According to Järveläinen et al. (2016), the stages of compression can be identified by using a relative density versus logarithmic pressure plot, a typical example of which is shown in Figure 6.5b. To produce this plot, the load is converted to a pressure and the extension is converted to a relative density using known values for the geometry of the piston and die, and the determined solid density. According to Järveläinen et al. (2016), during the initial stages of compression, the change in density is very small until the onset of breakage occurs. During this initial stage which in Figure 6.5b is between a Log[Pressure] of 0.001 – 0.3 MPa, the granules are rearranged, packed and deformed plastically. After this initial rearrangement phase, the relative density increases significantly. In Figure 6.5b this is between a Log[Pressure] range of 0.3 – 5 MPa. During this mid-stage, the compressive strength of the granules are exceeded and fracture occurs. At Log[Pressure]’s greater than 5 MPa, a small change in pressure leads to a substantial increase in the relative density. During this latter stage, the fractured granules are rearranged and packed. At the end of the compression process the granules are broken down into their primary particles and the powder compact is very close to its theoretical maximum packing density.

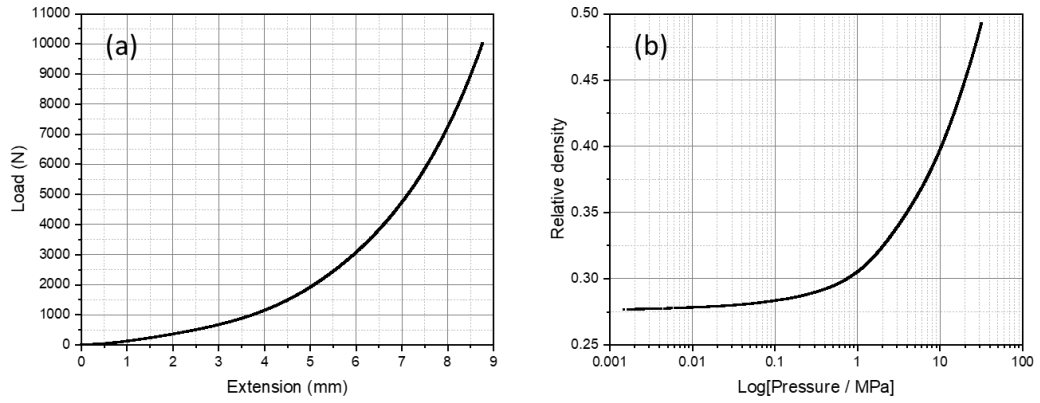


Figure 6.5 - Examples of typical compression curves obtained during confined uniaxial compression. (a) A typical load versus extension curve and (b) a typical Relative density versus logarithmic pressure curve.

Once the bulk compression data was obtained, the data was then analysed by the Adams and Kawakita models. These models simply relate powder bed volume reduction with the pressure applied during compression, whilst providing a measure for the agglomerate yield strength.

The Adams model was originally derived from the Mohr-Coulomb failure criterion and models the powder bed as a series of load bearing columns (Adams et al., 1994; Adams and McKeown, 1996). A full derivation of the Adams model is given in the work of Adams and McKeown (1996), the outcome of which is shown in Equation 6.12.

$$\ln P = \ln(\tau_0' / \alpha') + \alpha' \epsilon + \ln[1 - \exp(-\alpha' \epsilon)] \quad (6.12)$$

In Equation 6.12, P is the applied nominal pressure and ϵ is the natural strain which is given by Equation 6.13;

$$\epsilon = \ln\left(\frac{h_0}{h}\right) \quad (6.13)$$

where h and h_0 is the bed height and initial bed height of the powder in the die. In Equation 6.12, τ_0' is the apparent single agglomerate strength, which is related to the actual agglomerate strength via the proportionality constant k_1 (Equation 6.14).

$$\tau_0' = k_1 \tau_0 \quad (6.14)$$

In Equation 6.12, the quantity α' is the apparent coefficient of friction and is related to the pressure coefficient α , via the proportionality constant k_2 (Equation 6.15).

$$\alpha' = k_2 \alpha \quad (6.15)$$

The coefficient α' is also related to the initial powder bed aspect ratio, which has an effect on bed compressibility and is thought to be due to wall friction (Marigo et al., 2014).

Displayed in Figure 6.6 are the obtained Adams plots and the determined model constants obtained can be found listed in Table 6.2. The Adams model was shown to agree well and was capable of describing our experimental data with good correlation coefficients of 0.9830 – 0.9955 being obtained for the supplied powders.

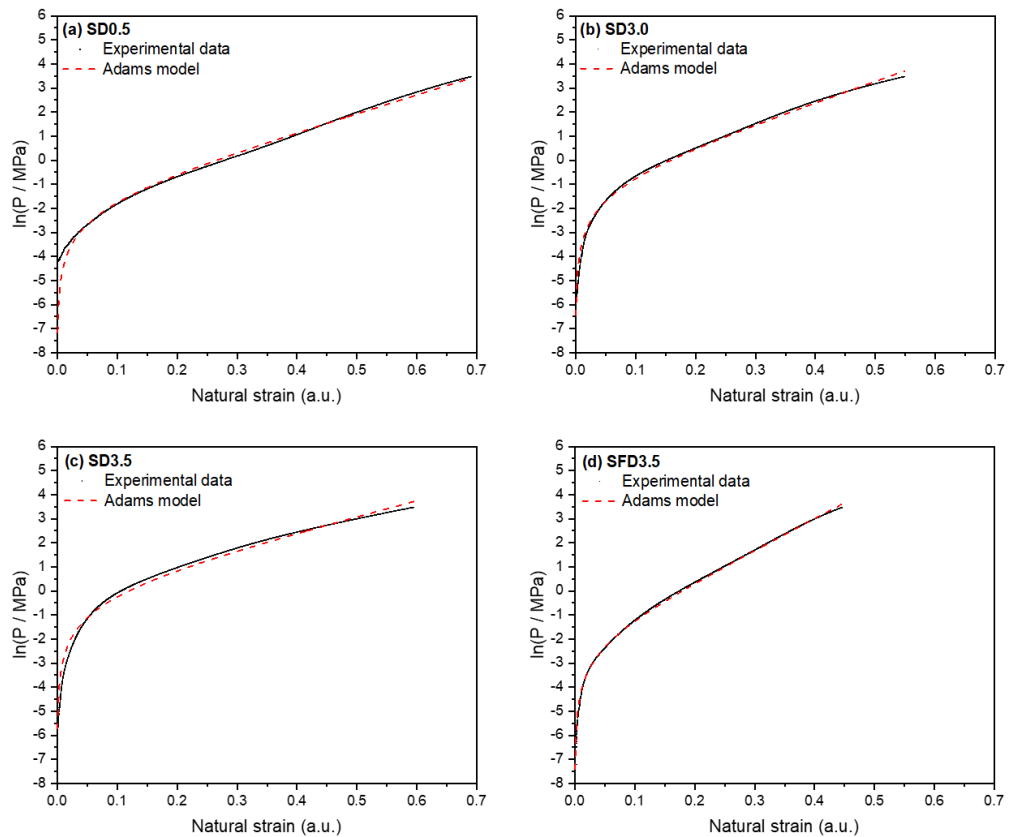


Figure 6.6 - Adams plots for spray dried and spin flash dried surface treated titanium dioxide.

Table 6.2 - Model constants obtained using the Adams model and bulk compression for spray dried and spin flash dried titanium dioxide.

Parameter	SD0.5	SD3.0	SD3.5	SFD3.5
α'	7.73 ± 0.02	8.81 ± 0.02	6.58 ± 0.02	13.20 ± 0.02
τ_0' (MPa)	1.131 ± 0.006	2.87 ± 0.01	5.50 ± 0.01	1.356 ± 0.005
R^2	0.9855	0.9926	0.9830	0.9955

The Kawakita model, Equation 6.16 describes the relationship between the pressure and the reduction of the powder volume and can be rearranged to give the linear form of the Kawakita model, Equation 6.17 (Kawakita and Lüdde, 1971);

$$C = \frac{V_0 - V}{V_0} = \frac{abP}{1 + bP} \quad (6.16)$$

$$\frac{P}{C} = \frac{1}{ab} + \frac{P}{a} \quad (6.17)$$

where C is the degree of volume reduction, V_0 is the initial apparent volume, V is the powder volume under applied pressure, P , a is a constant which is equal to the initial porosity and the constant b is considered to be related to the resisting forces of the powder to compression. In Equation 6.16 and Equation 6.17, $1/b$ has the dimensions of pressure and is related to the yield stress of the individual granules (Adams and McKeown, 1996).

The plots obtained from the application of the Kawakita model can be found displayed in Figure 6.7 and the Kawakita model constants can be found listed in Table 6.3. It must be noted here, that the Kawakita model was only applied to experimental data within the pressure range of 0.5 – 32 MPa as the data below a pressure of <0.5 MPa deviated from linearity. For all Kawakita plots, some non-linearity (curvature) was also observed at pressures >25 MPa. Despite this non-linearity, the Kawakita model gave good agreements with our experimental data as all plots gave R^2 values of 0.9933 – 0.9972.

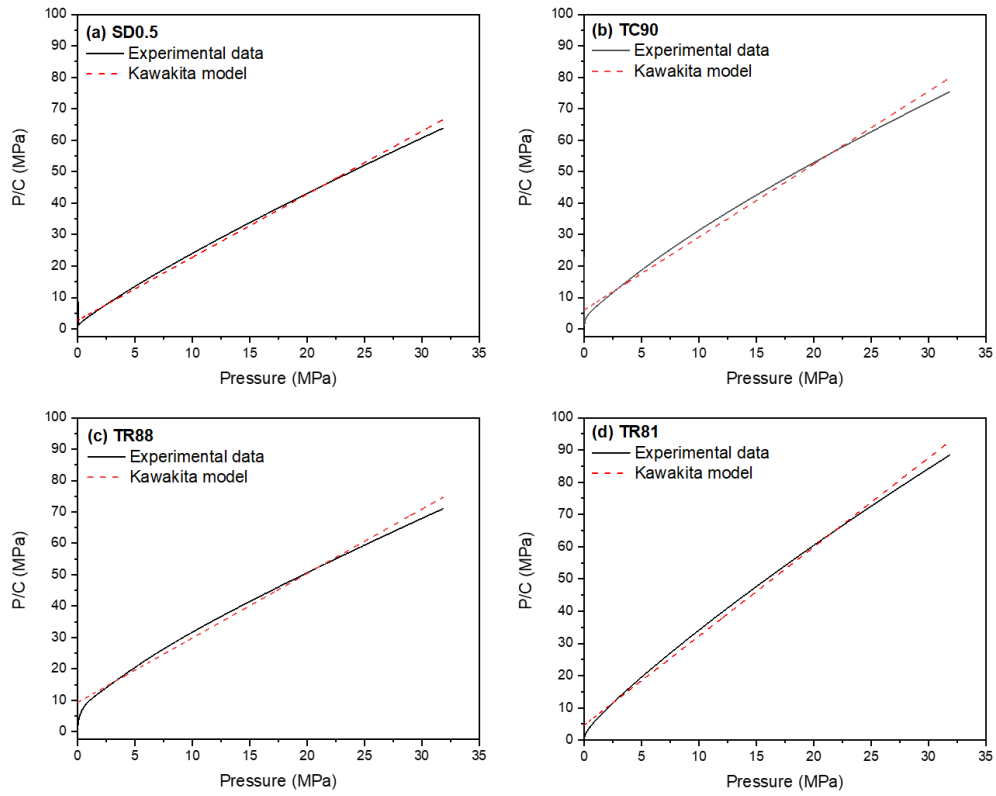


Figure 6.7 - Kawakita plots obtained for spray dried and spin flash dried surface treated titanium dioxide.

Table 6.3 - Model constants obtained when experimental bulk compression data of spray dried and spin flash dried titanium dioxide was analysed against the Kawakita model.

Parameter	SD0.5	SD3.0	SD3.5	SFD3.5
a	0.4988 ± 0.0005	0.4322 ± 0.0006	0.4876 ± 0.0006	0.3623 ± 0.0004
b (MPa ⁻¹)	0.729 ± 0.005	0.381 ± 0.001	0.219 ± 0.001	0.590 ± 0.006
$1/b$ (MPa)	1.372 ± 0.009	2.625 ± 0.007	4.57 ± 0.02	1.70 ± 0.02
R^2	0.9972	0.9941	0.9933	0.9964

The uncertainty with regards to the parameters k_1 and k_2 in the Adams model is known to make the interpretation of compaction data to determine single particle data somewhat difficult (Marigo et al., 2014). However, Adams et al. (1994) showed that the Kawakita parameter $1/b$ is proportional to τ_0' . Therefore in this work, these constants have also been compared. Figure 6.8 displays the correlation between $1/b$ and τ_0' values which were obtained in this work. The correlation between these constants were deemed to be good as a correlation coefficient of 0.9962 was obtained. For this study, this correlation also provides further support that the τ_0' is related to the agglomerate strength.

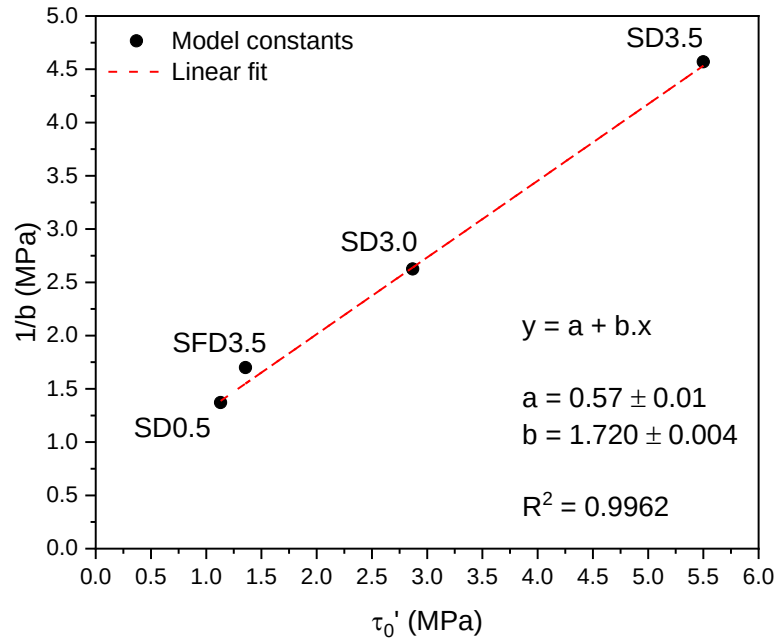


Figure 6.8 - The correlation between the reciprocal of the Kawakita parameter ($1/b$) and the agglomerate shear strength (τ_0') which is obtained from the Adams model.

6.3.4 Influence of size, composition and structure on granule strength and breakage

Based upon confined uniaxial compression results, it is apparent that the order of strength for the supplied powders is $SD0.5 < SFD3.5 < SD3.0 < SD3.5$. The order of breakability by impact is also expected to correlate with the granule tensile strength, which shows that SD0.5 is the most friable powder and SD3.5 is the least friable and is the most resistant to breakage. It is also worth mentioning, that the irregular shape of SFD3.5 is likely to impact the magnitude of its granule strength, since it is known that particles which are more irregular and less spherical give yield values which are lower (Wong and Pilpel, 1990; Xuehui et al., 2021). Wong and Pilpel (1990) found that the yield strength of irregular shaped particles could be reduced by as much as 20% in comparison to their spherical counterparts. Therefore, if the granules of SFD3.5 were more spherical, then the tensile strength obtained for SFD3.5 could be higher and this should be held in mind when interpreting the results for this powder. To gain further understanding to the strength and breakability of the supplied powders, it is also necessary to consider the influence of granule size, composition and structure.

Influence of granule size

To compare the strength of the supplied powders at the same particle size, it is necessary to correct the obtained strengths obtained from confined uniaxial compression. In this work, these

corrections were undertaken using Equation 6.18, which takes a similar form to Equation 6.2 presented earlier. Normally, Equation 6.18 is used during unconfined uniaxial compression experiments where a single granule is compressed between two platens. In this way, the maximum force required to break the granule is recorded and used to calculate the granules tensile strength. As reviewed, it is known that the tensile strength of granules decreases with increasing particle size, which is due to the fact that flaw sizes increase for larger granules. Therefore, if the force required to break a population of particles containing different sized granules was measured, an average value for the force would be obtained. Therefore in Equation 6.18, the value of kF_c can be seen as a constant and can therefore be used to correct the granule strength for other granule sizes. Therefore in this work, the influence of size was corrected for by using Equation 6.18 (Bika et al., 2001; Lister, 2016);

$$\sigma_c = \frac{kF_c}{d_g^2} \quad (6.18)$$

where σ_c is the corrected granule tensile strength, d_g is the granules diameter, F_c is the applied compression force and k is a parameter which depends on the size of the contact area between the agglomerate/granule and the platen, which usually has a value of 0.4 – 0.7 (Lister, 2016). These corrections were undertaken by first determining the value of kF_c from the experimentally determined values for the granule tensile strength and average granule size. During these calculations, the granule tensile strength was taken to be $\sigma_c = \tau_0'$, whilst the granule diameter was taken to be $d_g = d[v,50]$. With the value of kF_c determined, the tensile strengths of granules at specific sizes were then estimated for each powder. These estimations are displayed in Figure 6.9, which shows that when the powders are compared at the same size, the formulation/composition and structure of SD0.5 provides the lowest granule strength, whilst formulation/composition and structure for SFD3.5 provides the highest granule strength. Furthermore, this will mean that the composition and structure of SFD3.5 also provides the greatest resistance to breakage. Since the structure of SFD3.5, i.e. its porosity is fairly similar to the other three powders, the basis for greater granular strength for SFD3.5 must therefore be due to its composition, i.e. its higher level of surface treatment. It also appears that the order of granule strength for the other three powders correlates with surface treatment level.

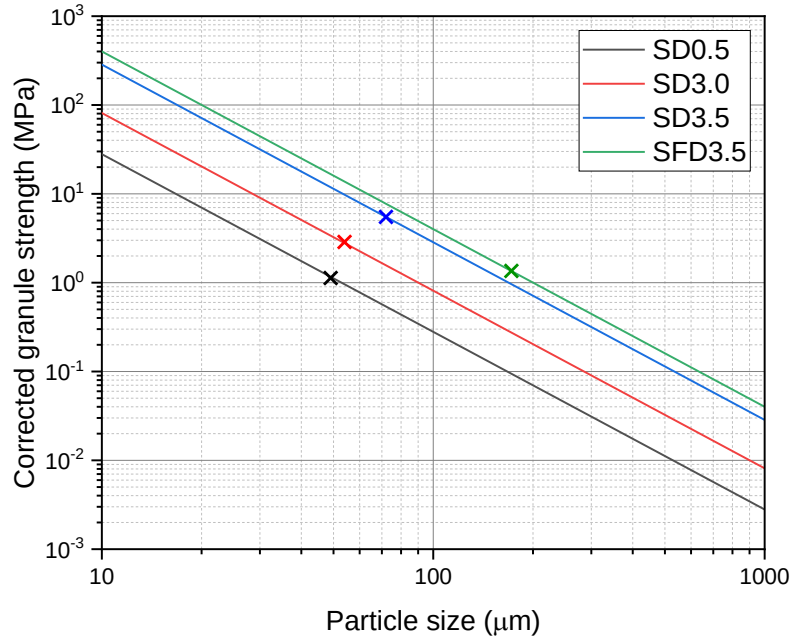


Figure 6.9 - Granule strength versus particle size for spray dried and spin flash dried titanium dioxide. Note: Crosses designate where τ_0' is located for each material.

Influence of formulation

To understand the influence of formulation (i.e. surface treatments) on granule tensile strengths, Rumpf's model for agglomerate strength was employed. Using this model, the solid bridge strengths were estimated by using known values for the corrected granule tensile strength, porosity, primary particle size and surface treatment solid fraction.

Rumpf's model for agglomerate/granule tensile strength is defined in Equation 6.19 and Equation 6.20 (Rumpf, 1962; Reynolds et al., 2005; Lister, 2016). In this model, the theoretical tensile strengths, σ_T for granules of the same size is suggested to be the summation of interparticle binding forces, F_b across the fracture surface which gives the following expression;

$$\sigma_T = nF_b \quad (6.19)$$

where n is the average number of interparticle contacts per unit area across the fracture surface. With a uniform primary particle size distribution, n is found to scale with the primary particle size, d_p and the granule solid fraction $(1 - \varepsilon_g)$. Equation 6.19 can therefore be rewritten as Equation 6.20;

$$\sigma_T = \frac{9}{8} \frac{(1 - \varepsilon_g)}{\varepsilon_g} \frac{F_b}{d_p^2} \quad (6.20)$$

where ε_g is the granules porosity. For solid bridges, the mean force, F_b binding the primary particles together (which in our case are the TiO_2 crystallites) can be defined by Equation 6.21 (Bika et al., 2005);

$$F_b = \pi r_{sb}^2 \sigma_{sb} \quad (6.21)$$

where σ_{sb} and r_{sb} is the solid bridge strength and its radius respectively. The radius of the solid bond can be obtained using Equation 6.22;

$$r_{sb} = 0.82 d_p \left[\frac{C_{solid} V_b}{\rho_p d_p^3} \right]^{1/3} \quad (6.22)$$

where C_{solid} and V_b is the wet solid concentration and volume of the bond respectively, and ρ_p is the density of the primary particles. Therefore, the term $(C_{solid} V_b)/(\rho_p d_p^3)$ essentially represents a ratio of the mass of the solid bonds, to the mass of the primary particles. In our case, this corresponds to the mass ratio of surface treatment to TiO_2 .

Using the determined material properties, σ_c for 50 μm sized granules, ε_g and d_p and Equations 6.20, 6.21 and 6.22, F_b , r_{sb} and σ_{sb} were calculated and can be found listed in Table 6.4. These estimations show that the binding force between the primary particles is increased with higher levels of surface treatment, which is highlighted by the values obtained for the binding force, F_b . A greater strength with higher binder content is also consistent with previous studies. With regards to the solid bridge strengths, it must be held in mind that the obtained values are scale dependent and must only be interpreted on a comparative basis. This is due to the fact that the number of bonds used in the Rumpf model are normalised by the area of the fracture plane. The composition of the solid bonds are also largely composed of alumina and therefore the values obtained for the solid bridge strengths should not be interpreted as being significantly different. According to the literature, the flexural (bending) strengths of alumina, silica and zirconia which are determined using a 3-point bend test are 277-425, 9-300 and 635-1200 MPa respectively (De Moraes et al., 2004; Madfa et al., 2014; Boniecki et al., 2020; Gafur et al., 2021; Zheng et al., 2021; Insaco, 2021). Furthermore, the flexural strength of ZTA (zirconia toughened alumina) which has a composition of 20% zirconia and 80% alumina is 150 – 643 MPa (Chuankrerkkul et al., 2016). ZTA has a similar composition to the composite zirconia alumina bridge, which is approximately 14% zirconia and 86% alumina. Therefore, since the flexural strengths of these materials do not vary significantly and no correlation can be found between the material and solid bridges strengths, it can be deduced that the values obtained for the solid bridges strengths are not significantly different.

Table 6.4 – Experimentally determined parameters and calculated parameters using Equations 6.15, 6.16 and 6.17 for 50 μm sized granules. Note: σ_c is obtained from the data displayed in Figure 6.9.

Property	SD0.5	SD3.0	SD3.5	SFD3.5
σ_c (MPa)	1.1	3.3	11.4	16.0
ε_g	0.243	0.247	0.293	0.240
d_p (nm)	266	297	297	315
F_b (nN)	20	85	370	446
r_{sb} (nm)	37	76	80	84
σ_{sb} (MPa)	5.1	4.7	18.6	19.9

Influence of structure

To understand the influence of structural properties, i.e. porosity and primary particle size on granule tensile strength, further estimations were undertaken using Rumpf's model. These estimations were made for 50 μm sized granules for samples SD0.5 and SD3.5, and can be found displayed in Figure 6.10, which shows corrected and estimated tensile strengths for samples SD0.5 and SD3.5.

The estimation shown for SD0.5 shows the influence that a larger primary particle size has upon granule strength, which when compared against the corrected value shows that when the primary particle size is increased from 266 to 297 nm, the granule strength does not change. This is likely due to the fact that a granule containing larger primary particles has fewer interparticle bonds, but as the primary particle size increases, then so does solid bridge radius resulting in a larger binding force between the primary particles in the granule. This means that when the primary particle size is increased, the binder which forms in the granule is shared amongst fewer solid bridges allowing the radius of the solid bridge to increase.

The estimation shown for SD3.5 demonstrates the effect that a reduction in porosity can have upon granule strength. When the porosity is reduced from 0.29 to 0.24, the granule strength for SD3.5 increases from 11.4 to 15.0 MPa. A greater granule strength with lower porosities is also consistent with the work of others. Also worthy of note, is the similarity between the estimated granule strength obtained for SD3.5 and SFD3.5 which has a granule strength of 16.0 MPa. The estimation obtained for SD3.5 suggests that if the porosity of SD3.5 was similar to SFD3.5, then SD3.5's granules would display a similar strength since these two powders contain similar levels of surface treatments. When compared at the same granule size, this estimation helps to provide further confidence that the strength of the supplied powders is governed by the level of the surface treatments found in each powder, which act as binders.

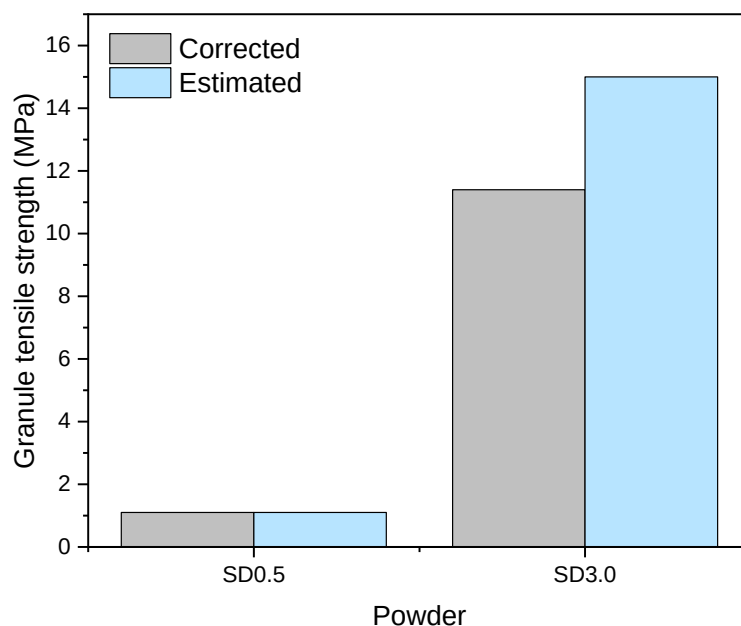


Figure 6.10 – Corrected and estimated granule strengths for SD0.5 and SD3.0. “Corrected” refers to granules tensile strengths which have been corrected on the basis of granules size from experimental data. For comparison, the granule size selected was 50 μm .

6.4 Conclusions

During conveying, particle breakage is undesirable as it can lead to a reduced particle size and a change in particle shape which leads to a deterioration in powder flow properties and hence bulk powder handling behaviour. Furthermore, it is known that breakage correlates with the bulk strength of the granules. Therefore, particle strength plays an important role in the bulk handling of particulate materials. The strength of granules and agglomerates are highly influenced by their composition and structure. Therefore in this work, the structure, strength and breakage of spray dried and spin flash dried titanium dioxide was investigated.

Using SEM, FIB-SEM, microtome sectioning and LF-NMR, the structure of the supplied materials were studied. The results showed that the supplied materials are assemblies of TiO_2 crystallites held together by solid bridges composed of alumina, and or silica/zirconia. Throughout the structure, networks of pores are present and the porosity of the supplied agglomerates were measured at values of 24.0 – 29.3%.

By applying confined uniaxial compression, the strength of the supplied powders were investigated and the order of strength was found to be $\text{SD0.5} < \text{SFD3.5} < \text{SD3.0} < \text{SD3.5}$. It is expected that the impact breakage of spray dried and spin flash dried titanium dioxide will also

correlate with granule tensile strength, since granule size, composition and structure have similar influences upon breakage during compression and impact.

To further understand the contributions to the strength and breakage of spray dried and spin flash dried titanium dioxide, the influence of granule size, composition (surface treatment) and structure (porosity and primary particle size) were considered. When corrected on the basis of granule size, the order of granule strength was found to be $SD0.5 < SD3.0 < SD3.5 < SFD3.5$ and this trend was attributed to the level of surface treatments present in these powders which provides strength. Hence, when the experimental data was analysed using Rumpf's model, a higher surface treatment level was found to produce stronger granules. For SD3.5, a higher porosity was also found to reduce this powders granule strength.

Based upon these findings, the strength of the supplied materials was explained. The lower strength of SD0.5 is likely due to its lower level of surface treatment, despite this powder having the smallest particle size. It appears that 0.5 wt% surface treatment is insufficient in providing adequate strength to this powder. Despite its higher level of surface treatment, the strength of SFD3.5 is significantly impacted by its larger mean granule size. As for SD3.0 and SD3.5, the higher alumina surface treatment level in these powders results in greater strength.

Overall, these findings are important for understanding the bulk handling behaviour of spray dried and spin flash dried titanium dioxide and furthermore, these findings are also important for predicting the strength of other potential spray dried and spin flash dried titanium dioxide powders.

Chapter 7 – Conclusions and further work

7.1 Conclusions

Particulate solids constitute a large proportion of raw materials, intermediates and products within the process industries associated with pigments, agricultural, food and pharmaceuticals. As all these materials have to be transported, handled or conveyed, there is an enormous need for information about their bulk handling characteristics. This research is concerned with the bulk handling behaviour of spray dried and spin flash dried titanium dioxide, which are commercial intermediates in the production of titanium dioxide pigments. These materials were kindly supplied by Venator, a leading manufacturer of titanium dioxide pigment. The aims and objectives of this research were to develop a greater understanding with regards to the bulk handling behaviour of spray dried and spin flash dried titanium dioxide. Consequently, this would involve understanding the factors, physical properties or composition which affected their bulk handling behaviour. Hence, this would allow the formulation-structure-property relationships for spray dried titanium dioxide to be developed. In order to develop this understanding, this study was therefore broken down into four main parts which were titled 1) Powder characteristics, 2) Powder flowability, 3) Adhesion and cohesion and 4) Structure, strength and breakage. Together, these four studies provided a comprehensive evaluation of the bulk handling behaviour of spray dried and spin flash dried titanium dioxide. In the discussions that follow, a summary of the main findings from each study is provided.

7.1.1 Summary of main findings

In the first study, the powder characteristics for spray dried and spin flash dried titanium dioxide was investigated in great detail. The main aim of this initial study was to characterise the physical properties of the supplied powders to support investigations in subsequent chapters. This work was reported in Chapter 3. During this first study, the supplied materials were characterised by scanning electron microscopy, laser diffraction, automated static image analysis, dynamic vapour sorption and nitrogen gas adsorption. These techniques were used to perform size and shape analysis, evaluate the moisture sorption characteristics and determine the specific surface area for the supplied materials. The size analysis determined the $D[v,50]$ of spray dried titanium dioxide to be 49 – 72 μm , whilst the spin flash dried material was determined to have a $D[v,50]$ of 172 μm . Shape analysis revealed that the spray dried powders featured spherical granules, whilst the spin flash dried granules were irregularly shaped. The size and shape differences were attributed to their respective drying methods. The moisture sorption analysis revealed that the materials were relatively dry with <1 wt% moisture being adsorbed at a relative humidity of 40%. Capillary menisci were also found to be absent during SEM analysis. Surface area measurements

determined SD0.5 to have a specific surface area of 8.1 m²/g, with SD3.0, SD3.5 and SFD3.5 measured at values of 18.7 – 21.9 m²/g. The moisture sorption and specific surface areas for the surface treated intermediates were also found to be consistent with values reported for similar materials in the literature.

In the second study, the powder flowability of the supplied materials were explored. This work was reported in Chapter 4. Throughout this work, the powder flowability was evaluated using several established methods. These methods included bulk and tapped densities, FT4 compressibility, static angle of repose, shear cell testing and the FT4 powder rheology. Several techniques were required to subject the supplied powders to a range of conditions and assess powder flow within the different powder flow regimes. Through the use of bulk and tapped density testing and compressibility tests, the density and packing was investigated under tapping and deformation revealing some of the unique characteristics for each powder, whilst indirectly assessing their flow behaviour. Static angle of repose, shear cell and FT4 powder rheology tests were then employed to study powder flow directly. Since the shape of the spray dried granules were exceptionally spherical, powder flow in all flow regimes were dominated by the influence of particle size and surface treatment level. A smaller particle size was thought to increase surface area allowing many more interparticle contacts to form, whilst a reduction in surface treatment was thought to increase the strength of the interparticle forces. Hence, powder cohesion was reduced for powders featuring larger particle sizes and higher surface treatment levels. Thus, greater cohesion resulted in poorer flow properties. In the Quasi-static flow regime, a more cohesive powder was found to increase friction and cohesion, whilst in the dynamic flow regime, a greater cohesiveness resulted in greater resistance to induced flow. A greater cohesiveness also enabled the powder to develop a greater strength upon consolidation and furthermore resulted in an unstable powder bed. With regards to the spin flash dried material, its larger granule sizes were found to be beneficial as a reduction in cohesion was observed, which resulted in this powder displaying higher bulk densities and better packing. However, its irregular shaped granules were found to impact its powder flow within all flow regimes by increasing friction, and this finding was attributed to the mechanical interlocking of its irregular shaped granules. Some powders were found to be sensitive to variable flow rates, but all powders displayed a similar sensitivity to aeration during FT4 powder rheology tests. During FT4 powder rheology work, evidence was also provided to suggest that the FT4 powder rheometer was capable of evaluating powder flow in the intermediate flow regime for the supplied materials.

To investigate the mechanism by which surface treatments influenced cohesion, a study dedicated to adhesion and cohesion was undertaken. This work was reported in Chapter 5, where a particle detachment method (drop test) was used to determine the cohesivity for the four powders. During these tests, particle adhesion results were found to correlate with surface treatment level, where a

higher surface treatment level resulted in lower adhesion. However, the drop test was unable to differentiate between powders with 3 or 3.5 wt% surface treatment levels. Since particle cohesion is influenced by the types of interparticle forces present, the degree of surface roughness and surface composition, particle cohesion was investigated further to work out the mechanism by which surface treatments were reducing cohesion. Since capillary menisci were absent and the supplied powders were relatively dry, van der Waals forces were considered to be the most dominant interparticle forces present as these forces are much stronger than the electrostatic interactions at small separation distances. With this in mind, surface chemistry and surface roughness were deduced to be the main factors influencing the strength of the van der Waal forces and hence the level of adhesion displayed by the particles in the drop test. Subsequently, atomic force microscopy was employed to investigate the contributions of these two factors, by utilising tapping mode analysis to investigate surface roughness and peak force tapping to examine adhesion. During this analysis, it was not possible to obtain data for the spin flash dried material. However, analysis of the spray dried particles revealed that these three powders exhibited a similar level of surface roughness and afterwards it was confirmed that the surface chemistry which was determined by the type and level of the applied surface treatment was governing the level of adhesion and hence the cohesion observed for these three powders. This analysis therefore showed that a higher level of alumina surface treatment reduced cohesion and by precipitating a small amount of silica prior to the application of 3.0 wt% alumina, the adhesion and hence cohesion could be reduced even further. During this chapter, a unique data analysis method was also employed to evaluate the critical diameter from the drop test.

In the final study, the structure, strength and breakage of spray dried and spin flash dried titanium dioxide was explored. This work was reported in Chapter 6. A study of breakage was required as particles can be subjected to fragmentation processes during handling, which leads to a change in the properties of the particulate material such as its mean particle size. Since breakage correlates with strength and strength is structure sensitive, SEM with microtome sectioning, SEM-FIB, LF-NMR and confined uniaxial compression experiments were utilised to characterise the structure, porosity and strength for the supplied materials. The initial qualitative analysis using SEM with microtome sectioning and SEM-FIB revealed that spray dried and spin flash dried titanium dioxide granules were not hollow. In fact, the granules were found to be composed of titanium dioxide crystallites, which were held together by the surface treatment, which acted as a binder, forming solid bridges between the titanium dioxide crystallites. Throughout the granule structures, networks of pores were detected and the porosity of the granules was determined to range between 24.0 – 29.3%. Noteworthy, the surface treatments were not found to influence granule porosity and the porosity of the spin flash dried material was not found to be significantly different in comparison to the spray dried granules. Unconfined uniaxial compression tests were

then applied to determine granule tensile strength. During this analysis, the Kawakita and Adams model was applied to the obtained force displacement data and Rumpfs model for agglomerate tensile strength was utilised to investigate the contributions of porosity and the surface treatments to the overall granule strength. Overall, this analysis revealed that an increase in surface treatment level led to an increase in granule strength. Other findings from this work showed that an increase in porosity by 5% would lead to a reduction in granule strength. Finally, it is expected that granules which are stronger will be more resistant to breakage by impact and compression since structure-strength relationships share similarities with structure-impact breakage correlations and furthermore, by the fact that breakage by compression and impact are known to subject particles to similar internal stresses.

7.1.2 Formulation-structure-property relationships

Based upon the findings of this work, it is clear that differences in particle properties and the formulation can result in substantial differences in bulk powder handling behaviour and it is clear that there are specific particle properties and formulations which are more desirable for better powder handling. Therefore, in the perspective of formulation and particle production, these findings can be used to inform manufacturing and be used to potentially improve bulk powder handling for spray dried and spin flash dried titanium dioxide. Furthermore, the findings of this work can also be used to predict how a new grade of powder may behave during processing, which is extremely valuable to industry.

With regard to particle properties, this work has drawn attention to three main physical properties which are beneficial to better powder handling and these properties should therefore be carefully controlled during powder production. These properties include granule size, shape and porosity. Considering particle size, a larger size was found to be beneficial for reducing interparticle friction and cohesion, and therefore is desirable for better flow properties. However, it is well known that larger granules have lower tensile strengths and as a result, are more susceptible to breakage. Therefore, unless sufficient strength can be imparted to the granules, a compromise would be required. As for particle shape, granules which are more spherical are advantageous as they significantly reduce friction, which is due to the fact that the possibility of particles interlocking is removed. For spray dried powders, the production of granules with spherical geometries is easily controlled during spray drying, however due to the mechanical method of slurry dispersion, control over granule shape is not possible with spin flash drying. For the respective drying techniques and powder production, control over granular shape should therefore be considered when better powder handling is required. With regards to porosity, a low granular void space is desirable for producing granules with higher tensile strengths as these particles are likely to display much better resistance to breakage, which is advantageous for improved powder handling.

The results from this study has also suggested that powder handling can be modified by changing the amounts and composition of the applied surface treatments. Whilst not their intended purpose, the use of surface treatments to improve bulk powder handling was found to occur via two main methods. The 1st method is through a reduction in powder cohesion by changing the surface composition/chemistry and the 2nd method is by increasing granule tensile strength which provides increased resistance to breakage. Considering interparticle cohesion, van der Waal forces will be the most dominant forces operating between dry powder particles. Therefore, the strength of these forces can be controlled by changing the surface chemistry. In comparison to TiO₂, alumina and silica have much smaller Hamaker constants and therefore, by applying these to the surface of TiO₂, the surface chemistry of the pigment can be changed to reduce interparticle cohesion. This means the amount of surface coverage and the type of surface treatment i.e. alumina or silica can be used as methods for reducing interparticle cohesion. The 2nd method by which bulk powder handling is improved via the use of surface treatments is due to their adhesive properties, where the surface treatments act as binders forming solid bridges between the TiO₂ crystallites within the granules. In a similar way to interparticle cohesion, granular strength can be altered by the amount of surface treatment. For example, by increasing the surface treatment level, more binder is present which forms granules with greater tensile strengths, which are more resistant to breakage. The surface treatments can therefore be used to improve powder handling by simultaneously reducing interparticle cohesion and increasing breakage resistance.

7.1.3 Implications for process behaviour and potential strategies

In light of the results obtained from this study, it is clear that the coating level has a significant impact on bulk powder handling behaviour. The process behaviour was significantly altered by the coating, at low coating levels higher levels of build-up and other handling issues were observed. The results from this study shows that this is due to the impact of coating on cohesion and on granule strength. Recalling the composition of the powder which causes the issue, the powder in question only contained 0.5 wt% alumina surface treatment, whilst other powders contained 3.0/3.5wt% surface treatments. Therefore, it appears that a 0.5 wt% alumina surface treatment is insufficient in reducing interparticle cohesion and insufficient in providing adequate granule strength.

Therefore, by addressing these aforementioned mechanisms, it could be possible to change the bulk handling behaviour of the material in question. Potential strategies could be focussed on addressing these mechanisms by making changes to the pre-coating and particle formation processes. For example, to reduce powder cohesion, the pre-coating process could be changed to improve coverage, which hence would reduce interparticle cohesion. Alternative coating techniques which provide better coverage could also be considered here. If acceptable, the coating

level could also be increased to 1.0 wt% especially if this composition is acceptable for the final application.

The literature review has also highlighted that there was some confusion with regards to the location of the aluminium dopant within TiO_2 crystallites. Some authors reported that the aluminium dopant resided within the bulk of the crystallite, whilst others stated that the aluminium dopant was present at the surface of the TiO_2 . A further study showed that the aluminium dopant resided under the surface of the TiO_2 and the wet milling process could erode away the surface titania and expose the alumina which was present underneath. Therefore, the TiO_2 production and milling processes could be optimised to produce TiO_2 crystallites with surfaces enriched with alumina, which could therefore help to reduce cohesion for TiO_2 powders featuring low levels of surface treatments.

To improve granule strength and increase breakage resistance, the drying processes could be modified or refined to produce granules which have lower porosities. Hence, a lower porosity would increase granule strength and increase breakage resistance. It could also be worth considering methods which maximise the amount of coating which ends up in the final granule as opposed to being loose in the final powder. This is because, these methods would be advantageous for increasing granule strength and breakage resistance. Alternative methods to spray drying and spin flash drying which produce stronger granules utilising the same formulations could also be considered here. However, it is worth mentioning, that it is ideal to have weaker granules as these granules need to be broken up in the final micronisation stage to make the final product. Furthermore, weaker granules are also better for reducing energy consumption in the micronisation process. Therefore, strategies aimed at reducing interparticle cohesion should be the key focus.

7.2 Limitations of this study and potential further work

Whilst this study is highly comprehensive and has addressed numerous questions, a number of further questions have been identified.

With regards to the formulation-structure-property relationships many of these correlations were developed. However, the exact mathematical relationships are not known. For example, it is known that an increase in coating level leads to reduction in cohesion, however the exact relationship, for example; linear or exponential etc is not known. Therefore, establishing these mathematical relationships could be extremely valuable for the design and development of further spray dried titanium dioxide particles. Experimentally, these unknowns could be addressed through the use of a lab scale spray drier, which could be used to prepare a series of powders with various coating levels, for example; 0, 0.3, 0.5, 1.0 and 3.0 wt% alumina coating levels. With further analysis of these samples, the exact mathematical relationships could therefore be

established. In fact, this approach has already been used by Li (2019), who prepared spray dried titanium dioxide powders with and without alumina surface treatments. However for this study, this approach was not utilised as it would not allow a relationship between process behaviour and lab scale testing to be developed. Nevertheless, this approach is suggested here to further refine the formulation-structure-property relationships for spray dried titanium dioxide.

Whilst particle strength measurements provide a good indication as to whether a powder is more or less susceptible to impact breakage, it would also be useful to measure the impact breakage directly. A potential technique which could be used to evaluate the impact breakage for cohesive powders such as spray dried titanium dioxide could employ the Malvern Mastersizer and the Scirroco dry powder dispersion unit. Unique feature of the Scirroco dry powder dispersion unit, is through this set-up's functionality whereby powders can be subjected to impact breakage at the bend of a pipe before having its particle size measured. Furthermore, the dispersion pressure of the Scirroco unit can be varied to increase or decrease the impact velocity. In fact this method has already been employed by others to study the impact breakage of granular materials, for example see Ali et al. (2015) or Bonakdar et al. (2016). However to the best of our knowledge, this technique has not been employed to relate formulation, structure and properties of similar grades of powders in order to investigate breakage behaviour.

Obtaining more data on the micro-mechanical properties of spray dried titanium dioxide would also be extremely valuable to understanding the breakage for spray dried titanium dioxide. In the literature, mechanical properties such as hardness and fracture toughness are known to be key properties which can affect breakage of granular materials, and these micro-mechanical properties can easily be determined using nanoindentation. In fact, this technique has already been employed to study the micro-mechanical properties of granular materials, for example see Schilde and Kwade (2012) or Schilde et al. (2012). Therefore, experiments involving the use of nanoindentation could be extremely valuable not only to this research, but also to academia (the study of powder technology) for understanding the breakage behaviour of granular materials.

This research has also mainly focussed upon understanding the influence of formulation, structure and particle properties, however it would also be useful to understand the influence of temperature and the relative humidity on the bulk handling behaviour. This is because these environmental factors can affect the powder moisture content, which may play a role on the flowability and cohesion for spray dried titanium dioxide.

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Appendix

Chapter 3 – Influence of sieving on particle size distributions

Displayed in Figure A3.1 are particle size data for as supplied powders and powder passed through a 500 μm sieve. This data therefore shows the influence that sieving has upon the particle size distribution for spray dried titanium dioxide. As can be observed, sieving has very little influence on the particle size distributions for the spray dried samples.

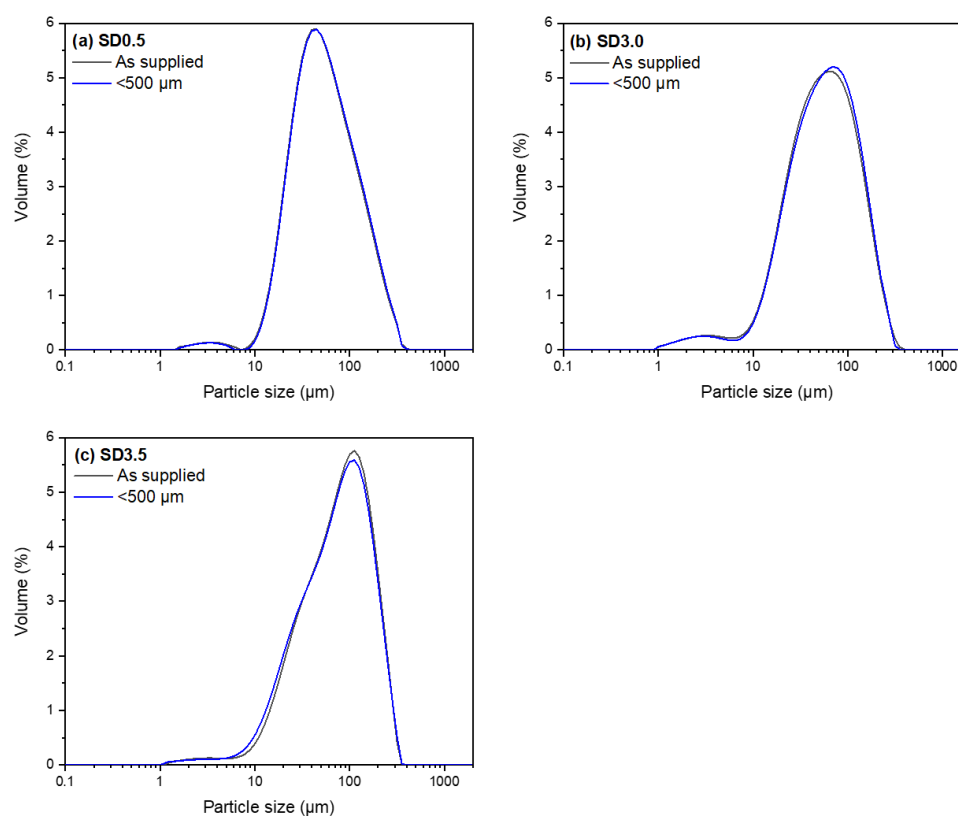


Figure A3.1 - Particle size distributions obtained for the powders as supplied and after passing the powders through a 500 μm sieve.

Chapter 3 – Nitrogen sorption isotherms

During Chapter 3, nitrogen sorption data was obtained during surface area analysis. The nitrogen sorption isotherms obtained from this analysis are therefore displayed in Figure A3.2 for the readers interest.

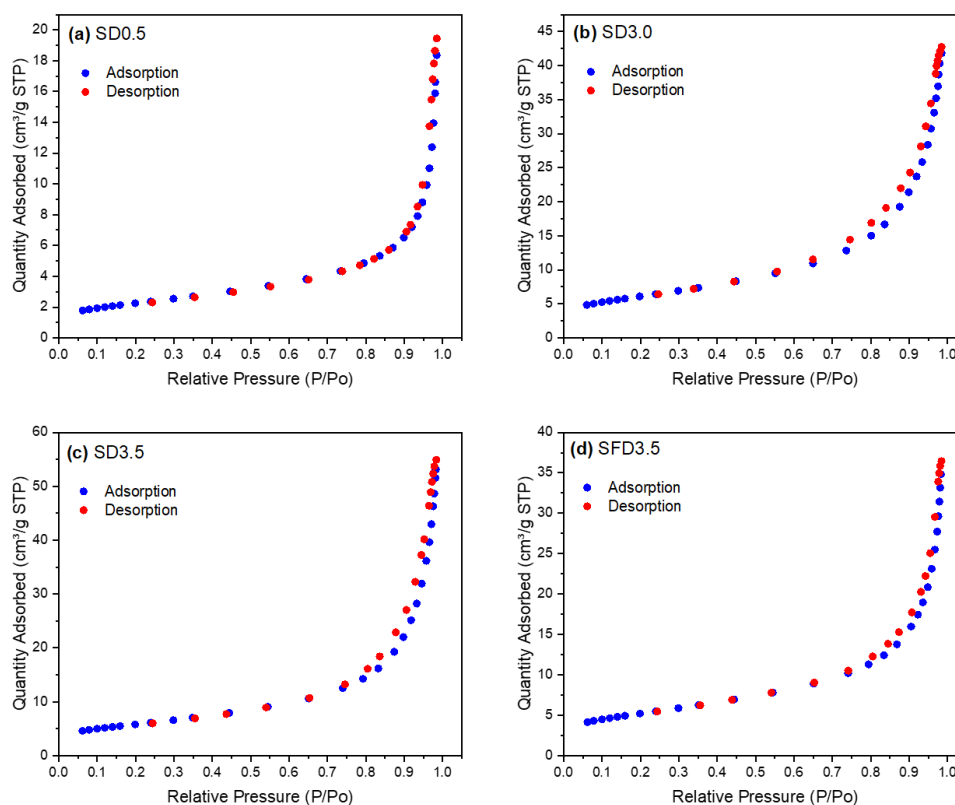


Figure A3.2 - Nitrogen adsorption isotherms for spray dried and spin flash dried titanium dioxide.

Chapter 3 – Dynamic vapour sorption isotherms

In Chapter 3, the presence of hysteresis loops were detected in some materials. To show the absence of a hysteresis loop in SD0.5, the y-axis has been re-scaled.

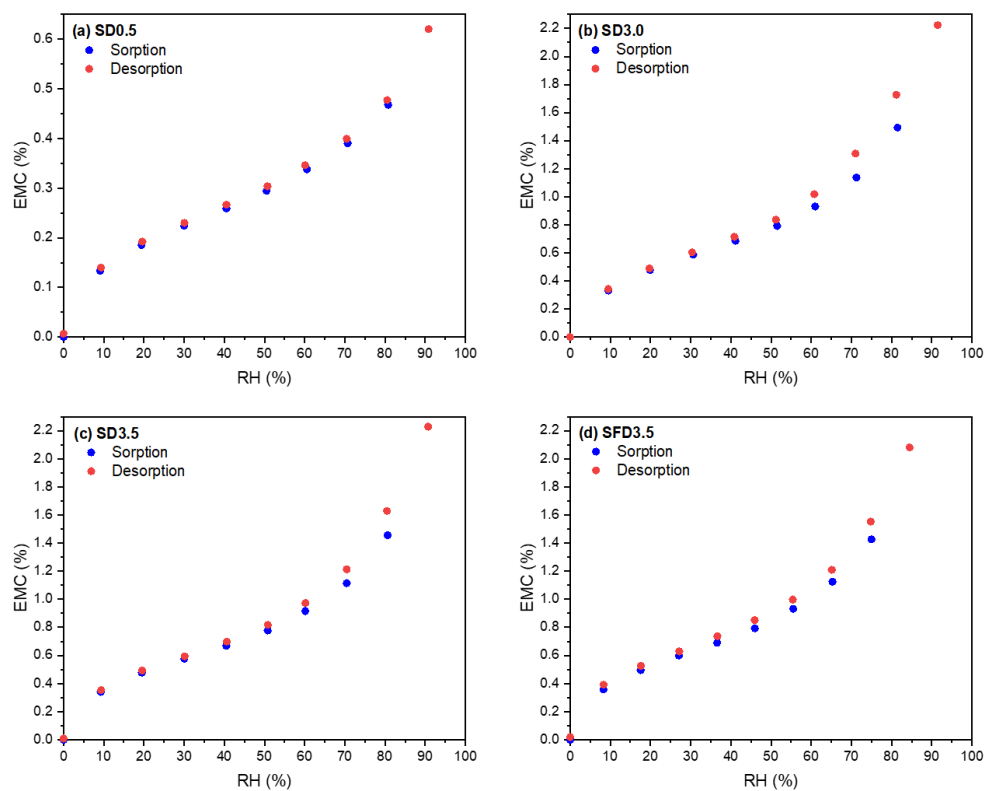


Figure A3.3 - Dynamic vapour sorption isotherms for spray dried and spin flash dried titanium dioxide. Note – The y-axis of SD0.5 (a) has been re-scaled to show the absence of a hysteresis loop.

Chapter 3 - Crystallite size analysis

To establish the TiO₂ crystallite sizes for each powder, size analysis using image analysis was undertaken. During this analysis, 450 – 550 particles were sized from 5 - 10 micrographs. The results from this analysis can be found displayed in Figure A3.1 and Table A3.1. The results from the analysis showed that crystallite size for SD3.0, SD3.5 and SFD3.5 were very similar with a $D[v,50]$ of 297 – 315 μm . However, the crystallite size of SD0.5 determined to be have a $D[v,50]$ of 266 μm and were therefore found to be slightly smaller.

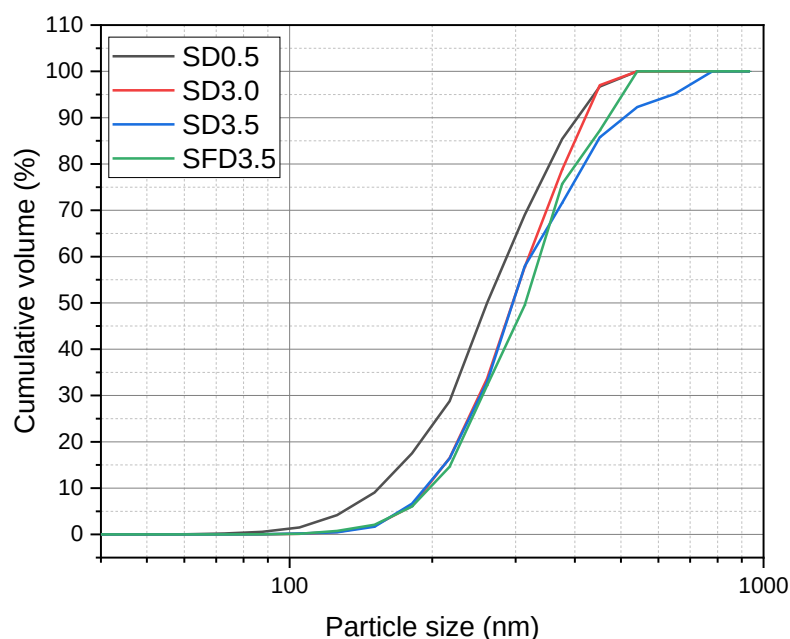


Figure A3.4 - Crystallite size analysis for spray dried and spin flash dried titanium dioxide.

Table A3.1 - Crystallite size analysis for spray dried and spin flash dried titanium dioxide.

<i>Powder</i>	<i>D[v,10]</i> (μm)	<i>D[v,50]</i> (μm)	<i>D[v,90]</i> (μm)	<i>Span</i>	<i>D[4,3]</i> (μm)	<i>D[3,2]</i> (μm)
SD0.5	154	266	406	0.95	292	255
SD3.0	195	297	372	0.60	325	300
SD3.5	194	297	510	1.06	345	307
SFD3.5	198	315	471	0.87	342	310

Chapter 4 – Schulze shear cell yield loci data

During Chapter 4, shear cell testing was undertaken to study powder flowability in the Quasi-static flow regime. During this analysis, flowability data was obtained at four pre-consolidation stresses; 1, 3, 5 and 7 kPa. For pre-consolidation stress, yield loci data was collected and this data is reported in Table A4.1 for the readers interest.

Table A4.1 - Parameters obtained from shear cell testing for spray dried and spin flash dried titanium dioxide.

<i>Sample</i>	σ_P (kPa)	ϕ_i (°)	c (Pa)	ϕ_e (°)
SD0.5	1	29 ± 3	126 ± 17	34 ± 3
	3	28.3 ± 0.9	367 ± 23	34 ± 1
	5	29 ± 1	639 ± 67	34 ± 2
	7	28 ± 1	889 ± 85	34 ± 2
SD3.0	1	27.3 ± 0.4	84 ± 3	31.1 ± 0.4
	3	26.3 ± 0.4	212 ± 12	29.6 ± 0.4
	5	26.1 ± 0.3	358 ± 1	29.4 ± 0.5
	7	26.5 ± 0.4	508 ± 11	29.8 ± 0.4
SD3.5	1	23.8 ± 0.9	35 ± 2	26 ± 1
	3	24.7 ± 0.2	98 ± 10	26.7 ± 0.3
	5	24.8 ± 0.8	242 ± 79	26.7 ± 0.8
	7	24.9 ± 0.5	234 ± 23	27.0 ± 0.5
SFD3.5	1	29.7 ± 0.9	93 ± 4	34 ± 1
	3	29.8 ± 0.9	241 ± 8	34 ± 1
	5	29.6 ± 0.3	400 ± 20	33.5 ± 0.3
	7	30 ± 1	572 ± 5	34 ± 1

Chapter 4 – Particle sizing before and after shear cell and FT4 powder rheology testing

Breakage during shear cell testing and FT4 powder rheology was also considered during Chapter 4 by analysing the particle size distribution of the powders before and after testing. The obtained data showed that no changes in the size distribution data occurred, which therefore indicated breakage did not take place.

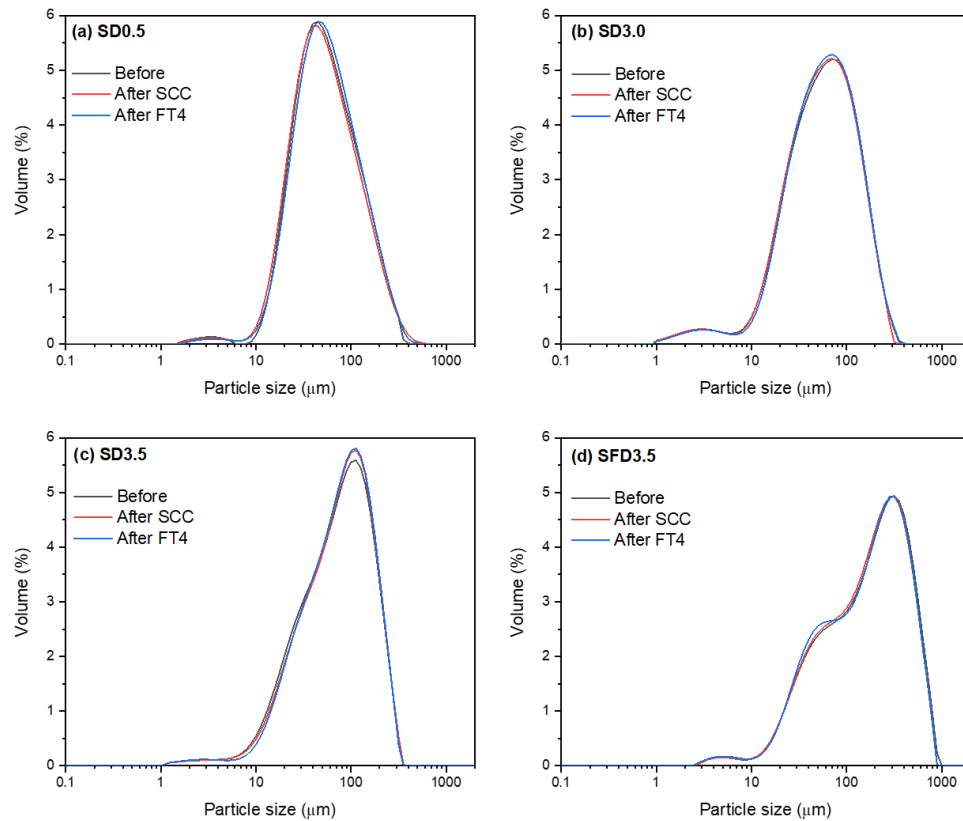


Figure A4.1 - Particle size distributions before and after Schulze shear cell (SSC) and FT4 powder rheology tests. Distributions after testing show no significant changes which indicates significant granule breakage did not occur.

Chapter 4 – FT4 blade height versus force profiles

In Chapter 4, the blade versus torque profiles obtained from the FT4 powder rheometer were analysed for stability. From these profiles, force data was extracted for a height of 15 mm. Displayed in Figure A4.2 is the complete data sets for the height versus force profiles for the FT4 stability test. Better unification of the data points between each test indicates much better powder bed stability, whilst a poor unification of the data points suggests poor powder bed instability. As can be observed in Figure A4.2, the data points for SD0.5 do not unit onto a single curve, therefore SD0.5 has poor powder bed stability.

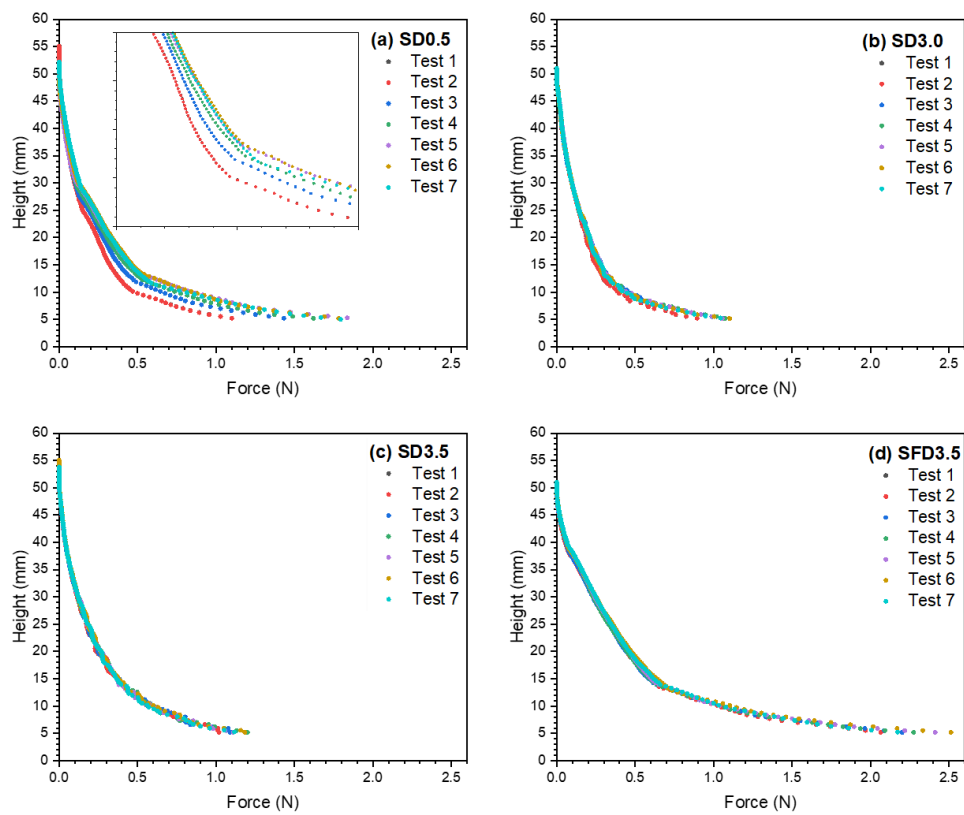


Figure A4.2 - Blade height versus measured force profiles obtained from FT4 powder rheology stability tests. Better unification of the data points between each test indicates much better powder bed stability, whilst a poor unification of the data points suggests poor powder bed instability.

Chapter 4 – FT4 blade torque versus height profiles

During Chapter 4, the blade torque versus height profiles obtained from the FT4 powder rheometer for the variable flow rate test program (test cycles 8 – 11) were analysed to provide evidence for stress-strain relationships. The complete blade torque versus height profiles are displayed in Figure A4.3. From these profiles, for test cycles 8 – 11, blade torque measured at a height of 15 mm was extracted and plotted versus tip speed to demonstrate that stress-strain relationships are present, and identify the flow regime in which the FT4 powder rheometer operates in.

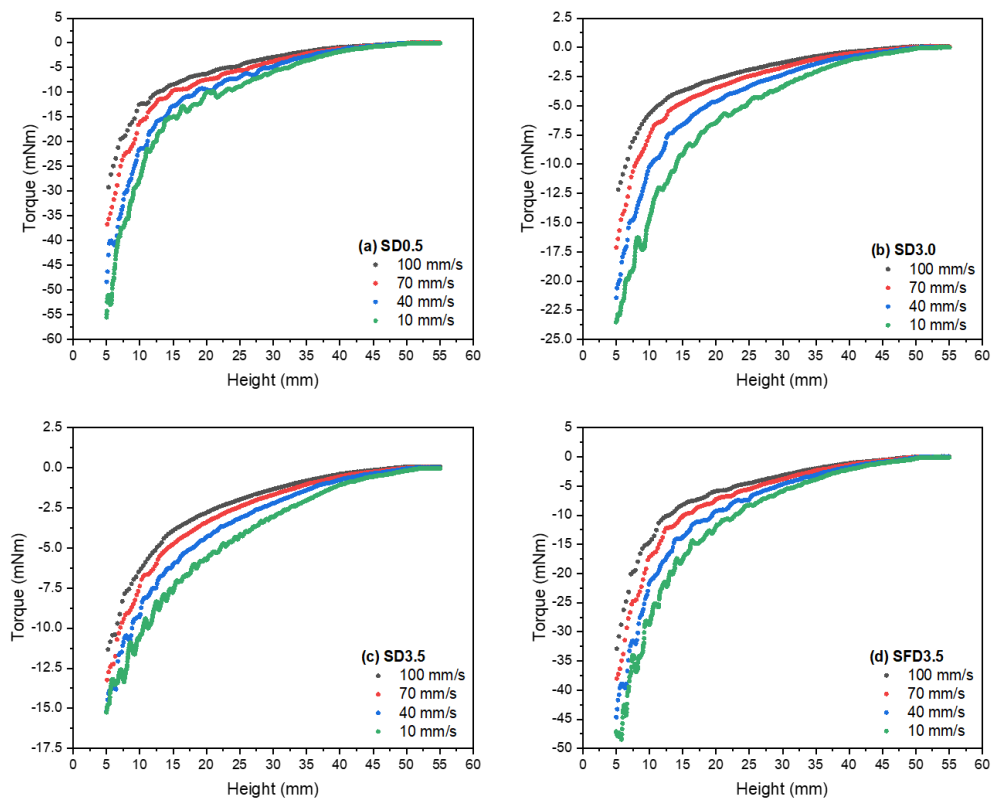


Figure A4.3 - Blade torque versus height profiles for blade tip speeds of 10 - 100 mm/s. **Note:** Since data points between different tip speeds do not unite, profiles indicate stress-strain relationships exist, which is a characteristic of the dynamic flow regimes (Intermediate and rapid granular flow regimes).